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Yhteenveto: Järvien ainetasemallien kehittäminen

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ISBN 951-47-3098-4
ISSN 0783-9472

Helsinki 1990. Valtion painatuskeskus

# Contents

# DEVELOPMENT OF MASS BALANCE MODELS FOR LAKES

Tom Frisk

FRISK, T. 1989. Development of mass balance models for lakes. Publications of the Water and Environment Research Institute. National Board of Waters and the Environment, Finland. No. 5.

A system of mass balance models for lakes was developed which included different hydraulic and kinetic descriptions. The hydraulic descriptions were the continuously stirred tank reactor (CSTR) and two modifications of the plug flow reactor (PFR), one with no additional input and one with additional input. A combination of CSTR and PFR was also treated. First and second order sedimentation kinetics were included in the model modifications and both voluminal and areal versions were considered. In voluminal versions the sedimentation is assumed to be proportional to volume, in areal versions to surface area. The models were tested against phosphorus data of Lakes Haukivesi and Päijänne, both situated in central Finland. The lakes are elongated and there is regional variation of water quality. Two different sub-basin divisions were used for both lakes. In the calibration results the differences between the calculated and observed phosphorus concentrations were not great. The best agreement was in most cases achieved when plug flow with additional input together with second order sedimentation kinetics was applied. The values of the calibrated sedimentation coefficients were dependent on the hydraulic description selected. There is a critical point for the monitoring of a lake (or sub-basin) at which measurements give the same sedimentation coefficient regardless of the degree of mixing used in the model. In calibration the average data of sufficiently long periods must be used in order to obtain reliable results of prediction with the models.

Keywords: Mass balance, modelling (-general-), reactors, phosphorus, lakes, Finland

## 1 INTRODUCTION

Monitoring of water quality is generally considered to be an essential part of environmental impact assessment today. In Finland about six hundred thousand water quality analyses of lakes, rivers, and coastal areas are made annually (Mäkelä 1988). Mass balance considerations have proved to be useful for obtaining information on the basis of these water analyses. In mass balance considerations data on both hydrological conditions and chemical quality of water are taken into account simultaneously. Thus it is reasonable to assert that monitoring of water quality should be replaced by moni-

toring of mass balances of watercourses.

However, monitoring of water quality (or mass balances) is not important *per se* but should be seen as a means of obtaining information for water management and water pollution control. Data on water quality is important e.g. for planning and supervision, but data alone is not sufficient unless methods for making quantitative assessments are available. Mathematical water quality models are such methods.

Water quality models can be either simple mass balance models or sophisticated conceptual models (e.g. Canter 1985). However, the distinction between these two model types is not always clear, and it may sometimes be difficult to decide whether a model is "simple" or "conceptual". For example all conceptual models are based on mass balance considerations. Simple mass balance models are often classified as black-box models because there are statistical components in these models or the basic assumptions are known not to be valid in a strict scientific sence, but they can produce results good enough when calibrated using sufficient data. Sophisticated conceptual models also have statistical (or black-box) components, for all ecological knowledge cannot be included in only one model.

In this study attention is paid only to simple mass balance models. Mass balance models and conceptual ecological models should be considered as different methodologies and thus it may be even somehow misleading to speak about *water quality models* when both model types are referred to. Some comparisons of these two approaches have been published in the literature (e.g. Scavia and Chapra 1977, Snodgrass 1979, Ahlgren et al. 1988). Both model types have their advantages and disadvantages, which will not be discussed here. However, the two approaches should not be seen as competitive alternatives but on the contrary they should be used as complementary methods. Thus a project in which a sophisticated model will be applied should be preceded by a project in which a simple mass balance model is used in the same case study area, carried out in a short time and requiring only few resources.

The development of microcomputers (personal computers) has made the use of mass balance models possible practically everywhere. These inexpensive computers can today operate even with very sophisticated programs. Although in efficient appliciations of sophisticated water quality models bigger computers are still necessary, personal computers are in all cases sufficient for mass balance models. There are today even pocket-size calculators that can manage most of the mass balance type water quality models.

There are many historical reviews of the development of water quality models. One of the most inspiring of these is the paper of O'Melia (1972) in which the approaches of Streeter and Phelps (1925) and Vollenweider (1969) were compared. The value of this comparison is increased by the fact that in 1972 when O'Melia's review was published the importance of Vollenweider's model was not at all as widely understood as it is today. Partly this is because the development of phosphorus retention models (e.g. Lappalainen 1974, 1975a, b, Kirchner and Dillon 1975) began only later.

O'Melia (1972) concluded that it was the short time elapse since the publishing of Vollenweider's (1969) paper that caused the difference in the degree of development of the model when compared with models of the Streeter-Phelps type. Although this was true to some extent, it is also the case that it is much easier to modify the Streeter-Phelps model to take into account the different factors acting in rivers. It is in many respects a conceptual model based on two well-defined processes and a hydraulic description (plug flow reactor) that is applicable to most rivers. The situation is not the same when the model of Vollenweider, preceded by the model of Piontelli and Tonolli (1964), is considered. In these models the realism in describing the (sedimentation) processes is not so important, and e.g. net sedimentation has been described using only one coefficient. In addition, the lake has been considered as totally mixed (i.e. as a continuously stirred tank reactor), which is not normally a realistic description. Thus the basic approach of these models is a black-box one and therefore it is unlikely that they could be developed so universally that they could yield good results in all or even almost all lakes. This does not mean that further development of this kind of models is impossible. The limitations as well as the conditions for the applicability of the models merely have to be taken into account. One advantage of this kind of models is that in the sense stated by Popper (1974) they are informative because they can easily be tested and thus also falsified.

No historical review will be presented here because models have been discussed earlier in this way e.g. by Dillon (1974), Golterman (1975), Frisk (1978), Frisk et al. (1981), Reckhow and Chapra (1983) and Ahlgren et al. (1988). The approach will be analytical instead of historical, i.e. the models will be discussed on the basis of their structure and characteristics. Some references will also be made to more sophisticated modelling approaches.

In Section 2 the background of the study is first presented and thereafter the aim of the study is given in detail. In Section 3 the theoretical devel-

opment of mass balance models is presented. Sections 4 and 5 include an empirical test of the different model versions. Both theoretical and empirical results of the study are discussed in Section 6.

# 2 THE STRUCTURE OF MASS BALANCE MODELS

## 2.1 General

The purpose of the development of a model must always be kept in mind in designing the model structure. In water management it is most important that the model is capable of producing reliable predictions. Predictions may concern e.g. the effects of the reduction of waste water loading or of changes in discharge conditions on water quality. In such cases the structure of the model may be simple, depending of course on the level of the resolution needed in the predictions. If the model is designed to be a tool for scientific research the demands are naturally different. The realism in the description of ecosystem processes is important, which may lead to very sophisticated model constructions.

In this section different structural features of mass balance models will be treated. The purpose is to give arguments justifying the approach of this study. In the analysis of mass balance models attention must be paid to hydraulic description and description of the behaviour of different substances in the water body. In the simplest mass balance models the internal (non-hydraulic) processes are described using only one retention term and this description requires special attention.

## 2.2 Hydraulic description

When hydraulic description is used in water quality models the main attention is paid to the description of mixing and dilution processes. Thus the "hydraulics" in such models constitute only part of the field of science called **hydraulics**. However, there are also water quality models in which the physical aspects are taken into account in a rather precise way. One excellent example of such models is that of Virtanen et al. (1986). This kind of three-dimensional modelling can produce very realistic information on the behaviour of the water body. However, the problem with such modelling is that its efficient use requires large amounts of empirical data for testing the ability of the model to predict variations in water quality. If such data cannot be obtained it is uncertain whether a sophisticated description of hydraulics gives additional information compared with simple models. This may be a question of contradictions. However, in future the development of computers as well as of aquatic science, especially limnology and hydrology, will make it possible to apply three-dimensional water quality models to all lakes and coastal areas that are important from the point of view of water management and water pollution control.

The simplest hydraulic description in water quality models is plug flow reactor hydraulics, abbreviated as PFR. PFR has traditionally been applied in river models since the days of the classical model of Streeter and Phelps (1925). In the ordinary form of PFR, in which no additional input from the drainage area of the river is allowed, the rate of change of material concentration equals the effect of local biological and physico-chemical processes in the water. Thus in the consideration of changes in water quality it is sufficient to follow the reactions in a certain defined body of water, the "plug".

In certain lakes the water flows in winter under the ice cover in the epilimnion just like in a river and so the PFR description is suitable. There are, of course, lakes that resemble rivers in their behaviour, the so-called river-run lakes (Chapra and Reckhow 1983). The applicability of PFR for elongated lakes is one of the topics of this study. The mathematical description of PFR will be given in Sections 3.3 and 3.4.

A very different hydraulic description of a water body is the analogy with a continuously stirred tank reactor, abbreviated as CSTR. For lakes this description has been generally applied since the 1960s (e.g. Biffi 1963, Piontelli and Tonolli 1964, Vollenweider 1969). The CSTR description is applicable for shallow lakes that are not stratified or for holomictic lakes during the turnover periods. For holomictic lakes this description has also been widely applied in steady-state considerations. The mathematical description of CSTR will be given in Section 3.2.

The limitations of these extreme descriptions have been overcome using two different approaches. In the first approach the spatial distribution of the substance concerned is described by an advection-dispersion equation. Both PFR and CSTR can be modified in this direction. In rivers there is always longitudinal mixing, which can be taken into account by adding a term describing the

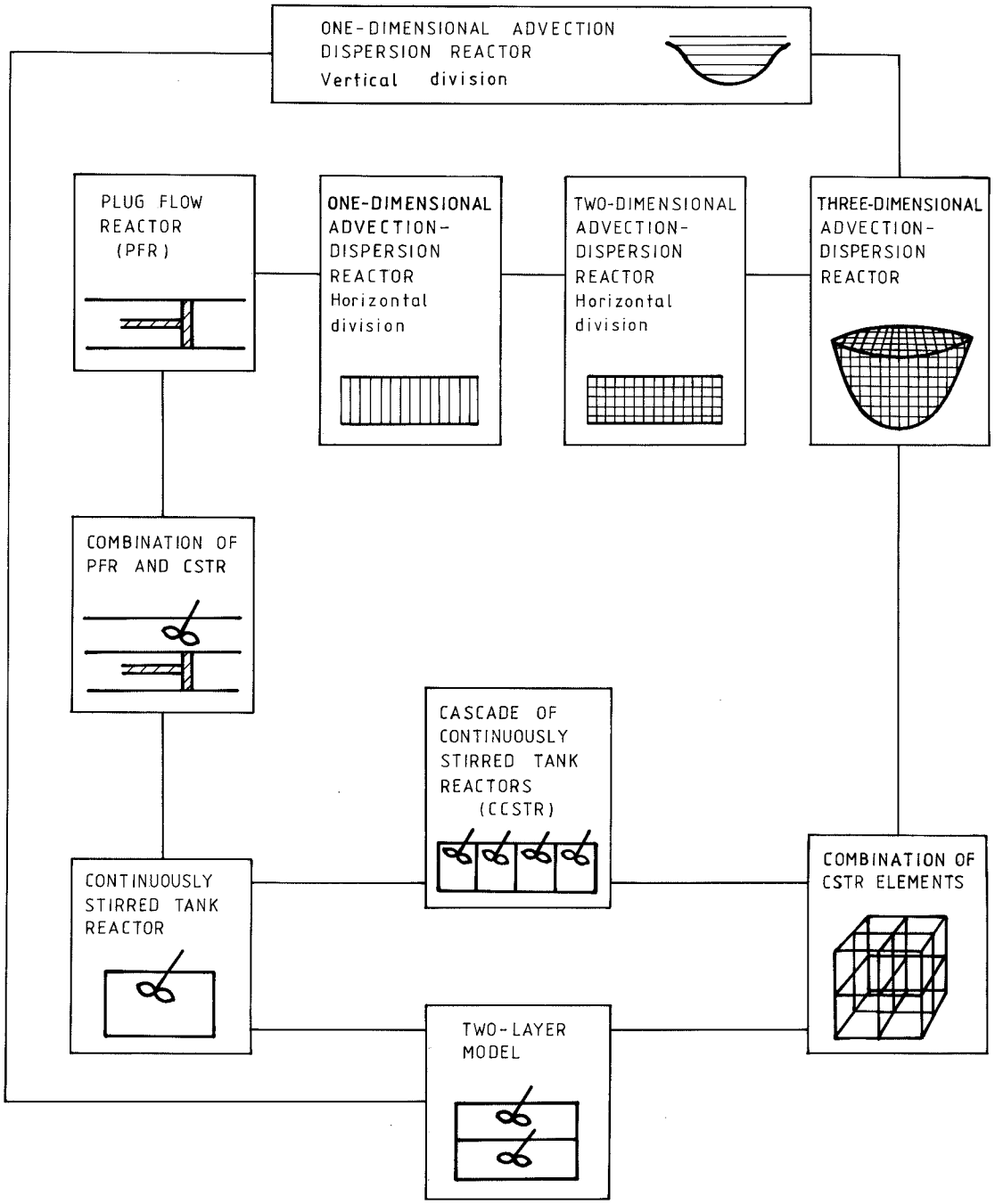



Fig. 1. The relationship between different hydraulic descriptions (i.e. descriptions of mixing and dilution) generally used in water quality models.

effect of dispersion into the plug flow equation. In lakes the vertical stratification is important and therefore the water body can be divided into slices, as for a solution of a vertical advection-dispersion equation (e.g. Chen and Orlob 1972) (Fig. 1).

The second approach is to combine several CSTR elements. Then a description of a two-layer CSTR model, one layer describing epilimnion and the other hypolimnion, or a cascade of continuously stirred tank reactors (CCSTR) is obtained. Elements can also be combined to describe the three-dimensional variation of water quality.

The advection-dispersion description can easily be applied as two-dimensional or three-dimensional versions (e.g. Virtanen et al. 1986). The three-dimensional advection-dispersion model is in many respects similar to the above mentioned three-dimensional combination of CSTR elements. In three-dimensional advection-dispersion models the degree of dispersion is regulated by the dispersion coefficient, while in the combination of CSTR elements the size and the number of the elements determine the degree of mixing unless special terms describing dispersive mass flows between the elements are applied (Fig. 1).

Although application of the different mixing equations is technically relatively easy, the problem with more than one-dimensional descriptions (as well as with dynamic one-dimensional descriptions) is determination of the velocity of flow at different points of the watercourse. For this purpose hydraulic current models must be employed. Such models are nowadays in routine use, but there is lack of specialists capable of applying them. When simple hydraulic descriptions are concerned, elementary water balance calculations are usually sufficient for determining the hydraulic and hydrological data needed in the models.

In order to get the best possible idea of the reaction rates in the aquatic ecosystem a hydraulic description as realistic as possible should be used. For these purposes it would be important to know the degree of dispersion exactly. Tracer techniques can be used (e.g. Kinnunen 1978) but in lake systems they may be expensive and time-consuming.

The coefficients that are obtained on the basis of observational data are essentially dependent on the hydraulic description used in the model. If there is insufficient empirical data on the systems to be studied a more sophisticated hydraulic description cannot provide more accurate estimations of reaction coefficients.

Another question, still connected with the same problem of empirical determination of reaction coefficients of the models, is that in dynamic model applications coefficients are not necessarily the same as in steady-state applications. However, in the planning of water resources often only routine monitoring data is available and the steady-state approach is used. It is not certain whether the application of sophisticated hydraulic descriptions can improve the accuracy of the estimations of reaction coefficients needed in these steady-state cases.

## 2.3 Water quality variables

In principle all water quality variables can be included in models. The difficulties in modelling certain variables may be due to the fact either that they are dependent on many other water quality variables which should be simulated simultaneously, or that there is not sufficient data enough for identifying the reaction kinetics of the substance considered.

In the oldest models, biochemical oxygen demand (BOD) and dissolved oxygen concentration (DO) were used as state variables (Streeter and Phelps 1925). These variables have preserved their status among the most important state variables. Since the 1960s total phosphorus has been the most common state variable in mass balance models. Thus it can be seen that the state variables tend to represent variables describing the changes caused by human activities (in this case oxygen deficit and eutrophication).

There are, of course, many other variables that are important from the point of view of water pollution control. In complex water quality models even several tens of state variables may be included (e.g. Park et al. 1974). In Finland a model called FINNECO with seventeen state variables was developed (Kinnunen et al. 1982) on the basis of the model originally developed by Chen and Orlob (1972) and later called EPAECO (Gaume and Duke 1975).

In this study attention is paid only to total phosphorus which can be used as a relative measure of eutrophication. Phosphorus-chlorophyll relationships have been traditionally applied in limnology (e.g. Sakamoto 1966, Megard 1972, Dillon and Rigler 1974b, Jones and Bachmann 1976, Ahl and Wiederholm 1977, Schindler et al. 1978, Edmonson and Lehman 1981, OECD 1982, Ostrofsky and Rigler 1987). Peters (1986) collected statistical models for predicting other biological variables on the basis only of total phosphorus, e.g. phytoplankton biomass (Watson and Kalff 1981), cyanobacteria (Smith 1985), zooplankton (Pace

1986), crustacean plankton (Hanson and Peters 1984), fish (Hanson and Leggett 1982) and primary production (Smith 1979). Although regression models of this type cannot give accurate results in all cases (cf. Eloranta 1985) the possibility of forming them indicates the importance of total phosphorus as a regulating factor in the lake ecosystem.

Phosphate phosphorus was not considered to be a variable exactly representing the share of phosphorus available to phytoplankton. Furthermore, simulation of phosphate phosphorus would also have required simulation of phytoplankton, which has proved to be difficult (e.g. Niemi 1986a, b).

Other possible state variables for mass balance considerations would have been nitrogen and organic matter. If nitrogen had been considered there would have been difficulties in the conceptual definition of the reaction coefficient (cf. Vollenweider 1969), due to the complexity of the nitrogen cycle. In addition, the practical importance of simulating total nitrogen may be questioned. The simulation of nitrogen fractions (ammonia, nitrite and nitrate) might be more reasonable, but the fractions cannot be simulated separately, nor without phytoplankton. Organic matter would have been a suitable and an important variable for mass balance considerations because humic substance are present in high concentrations in Finnish waters, today often increased by human activities. A steady-state model for humus was presented and applied to three lakes by Frisk and Pennanen (1986). However, there are not sufficient data on TOC or TOD from the case-study areas of this study and BOD, COD or colour were not considered as variables quantitatively describing organic matter.

## 2.4 Description of phosphorus retention

Phosphorus retention, which will be mathematically defined in Section 3.1, is by definition the difference between phosphorus input and output. The most important factor affecting phosphorus retention is net sedimentation, i.e. the difference between sedimentation and release from the sediment. Other factors also affect measured retention values, e.g. output of phosphorus from the lake in fish catch. Changes in the volume of the lake also have an effect on measured retention values, but they can normally be neglected when long periods of time are considered.

In describing phosphorus retention two different approaches have been widely applied. They can be called the **kinetic approach** and the **retention coefficient approach**. In kinetic approach the retention of phosphorus is described in the same way as a chemical reaction in the field of reaction kinetics. Thus retention is described proportionally to phosphorus concentration or as a function of phosphorus concentration. In the model of Vollenweider (1969) retention is described proportionally to the phosphorus concentration and the volume of the lake, whereas in the model of Chapra (1975) proportionality is assumed to the concentration and the surface area of the lake (theoretically the area of the sediment). These are first order kinetic models, in which retention is described as strictly proportional to concentration. The possibilities of using second or higher order models were already discussed by Dillon (1974). Frisk (1981a) proposed a more general kinetic desription in which retention was assumed to be proportional to concentration raised to power b where b is the **sedimentation exponent**. In Frisk's (1981 a) study the best agreement with empirical data was in most cases gained using the value 1.9 for b.

In the retention coefficient approach, retention is not described as a function of phosphorus concentration but of phosphorus input. The retention coefficient is defined as the ratio of retention to input. The principle of the retention coefficient was already included in the studies of Piontelli and Tonolli (1964), Vollenweider 1969, 1975 and Dillon and Rigler 1974a). However, these authors did not give any formulae for calculating the retention coefficient on the basis of lake characteristics (e.g. volume, area, dicharge). Such formulae, which can be called **empirical retention models**, were presented e.g. by Lappalainen (1974, 1975a, b, 1977), Kirchner and Dillon (1975) and Larsen and Mercier (1976). Later different versions of these models have been presented (e.g. Frisk 1978, Frisk et al. 1981). The applicability of different empirical retention formulae has been studied by Frisk (1978), Canfield and Bachmann (1981) and Frisk et al. (1981).

Among empirical retention models two groups can be separated. In the first group, including the models of Kirchner and Dillon (1975), Chapra (1975) and Larsen and Mercier (1976), the retention coefficient is calculated on the basis of only hydrological and morphometric data. This is equivalent to the assumption that the retention coefficient is not a function of phosphorus input and thus not of concentration. This also means that the corresponding first order kinetic coefficient is not dependent on concentration, i.e. this group of models is equivalent to the first order

kinetic models mentioned above. In the second group of models, including those of Lappalainen (1974, 1975a, b, 1977), Frisk (1978) and Frisk et al. (1981), the retention coefficient is dependent not only on hydrological and morphometric data but also on phosphorus input. These models resemble the above mentioned second order models (Fig. 2).

It is not easy to study empirically which description of retention is superior to others. The descriptions are always oversimplifications of reality. The retention models are not universal and no single model will be applicable to all lakes. One possible approach in the comparison of different descriptions is to use a large number of lakes and statistical analysis, as in the study organized by OECD (1982). In the study of OECD (1982) it was noticed that phosphorus retention becomes relatively higher at higher input values. The study of Canfield and Bachmann (1981) showed a similar relationship. On the basis of statistical analysis it thus seems that the first order model is not universally valid, as was already stated by Vollenweider (1969). In this study one of the topics is the order of the retention kinetics. Empirical retention models were not included, but the kinetic approach was chosen. For phosphorus the conservative description in which retention is assumed to be equal to zero is not realistic, and this description was considered only for the sake of comparison. First and second order versions were developed and tested for the different hydraulic descriptions.

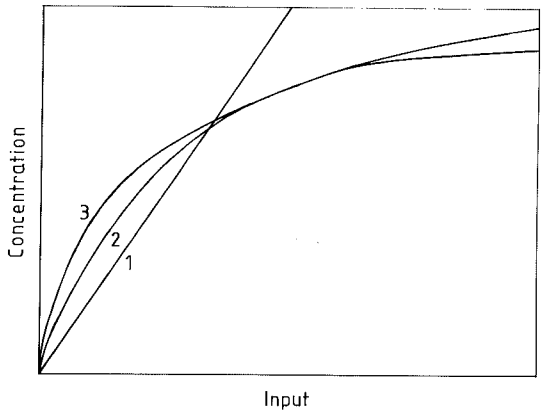



Fig. 2. The relationship between phosphorus input and the average concentration calculated using the first order model or the retention model of Kirchner and Dillon (1975) or Chapra (1975) (1), using the second order model (2), and using the model of Lappalainen (1974, 1975a, b, 1977) (3).

## 2.5 The aim of the study

In this study the main emphasis is on methodological aspects of obtaining information relevant for mass balance models used for water management purposes. However, sophisticated mathematical methods have not been applied, but the approach of this study is limnological, and the practical applicability of the results has especially been kept in mind. The following purposes were set to the study:

1. To present a system of mass balance models for lakes. In this study a systematic approach is applied. Some of the models presented here have been presented earlier by other authors or by the author of this study, but some of the modifications are new (at least in the context of lake modelling). The same kind of methodology has been applied in chemical engineering (e.g. Cooper and Jeffreys 1971, Denbigh and Turner 1971, Nauman and Buffham 1983, Westerterp et al. 1984). The hydraulic descriptions are the continuously stirred tank reactor (CSTR) and two versions of the plug flow reactor (PFR), and their combination. The internal processes (= the retention of phosphorus) are described by only one term, with first or second order loss reaction kinetics.
2. To calibrate different model modifications using phosphorus-balance data from two Finnish lakes. The lakes chosen for the calibration were Päijänne and Haukivesi. Both lakes are elongated in shape but their detention times differ considerably from each other. Phosphorus was chosen because it is an important factor causing eutrophication in both case study lakes, its description using simple kinetic equations is theoretically reasonable and sufficient balance data is available.
3. On the basis of empirical testing of the models to estimate the applicability of the different model modifications.
4. To provide information on the magnitude of the values of the reaction rate coefficients in different model modifications.
5. To investigate the relationship between the hydraulic description of the model and the reaction rate coefficient estimated on the basis of observational data.
6. On the basis of empirical and theoretical study, to present some considerations of importance from the point of view of applying kinetic mass balance models in water management contexts.

# 3 DIFFERENT MASS BALANCE MODEL TYPES — FURTHER DEVELOPMENT OF THE THEORY

## 3.1 Basic concepts

In this section the basic concepts of mass balance models presented and developed in this study will be defined. The most practical way to do this is to consider the general mass balance equation for a lake or a part of a watercourse:

$$\frac{dm}{dt} = I - O - S \quad (1)$$

where
m = total amount of the substance considered in the water body (M)
t = time (T)
I = total input of the substance considered ($M\ T^{-1}$)
O = total output of the substance considered ($M\ T^{-1}$)
S = effect of the internal (= non-hydraulic) processes on the amount of the substance considered ($M\ T^{-1}$)

The average concentration is defined as follows:

$$c = \frac{m}{v} \quad (2)$$

where
c = average concentration of the substance considered in the lake or the water body ($M\ L^{-3}$)
V = volume ($L^3$)

On the basis of Eq. (2) Eq. (3) can be written:

$$\frac{dm}{dt} = V\frac{dc}{dt} + c\frac{dV}{dt} \quad (3)$$

In short-term considerations of mass balances variation of the volume must be taken into account, whereas in long-term considerations it can normally be neglected and the basic equation (1) can be written as

$$\frac{dc}{dt} = \frac{I}{V} - \frac{O}{V} - \frac{S}{V} \quad (4)$$

In mass balance studies steady state is defined as follows:

$$\frac{dm}{dt} = 0 \quad (5)$$

which means that the average amount of the substance in the lake remains constant. In strategic planning the average concentrations are usually used and therefore steady-state versions of mass balance models have been considered especially important. The steady-state mass balance equation is the following:

$$S = I - O \quad (6)$$

The total input (I) is defined as the sum of all external mass discharges. Thus it consists of the following factors:
— inputs of rivers
— effect of nearest drainage area
— input of precipitation
— input of waste waters

In the context of certain model modifications the terms **initial input** and **additional input** will be introduced. These concepts are practical when elongated lakes are considered. Initial input is the input coming along the main river (possibly incremented by the point loads discharging into the uppermost part of the lake basin) or the input from the preceeding sub-basin. Additional input, usually expressed as mass per time and per length of the basin, is the mass discharge coming straight from the drainage area as well as with the precipitation. The additional input comprises both natural leaching and the diffuse loading caused by human activities.

The internal input from the sediment is included in the S-term of Eq. (1).

The output (O) means the output of the outlet (or the outlets) of the lake. All the other output factors, especially sedimentation but also the effect of evaporation and output with animals (e.g. fish) are included in the S-term of Eq. (1).

The S-term of Eq. (1) is the net effect of all the internal reactions decreasing the amount of the substance. Retention of the substance is defined as the difference between the input and the output:

$$S_{ret} = I - O \quad (7)$$

where
$S_{ret}$ = retention ($M\ T^{-1}$)

Thus, according to Eqs. (6) and (7), retention at steady state equals the total effect of the internal reactions. If phosphorus is considered, the most important reactions are the exchange reactions between the water body and the sediment. Net sedimentation is defined as the difference between gross sedimentation and release from the sediment:

$$S_{ns} = S_{gs} - S_r \quad (8)$$

where
$S_{ns}$ = net sedimentation (M $T^{-1}$)
$S_{gs}$ = gross sedimentation (M $T^{-1}$)
$S_r$ = release from the sediment (M $T^{-1}$)

Retention coefficient is defined as follows:

$$R = \frac{S_{ret}}{I} = \frac{I - O}{I} \quad (9)$$

where
R = retention coefficient (dimensionless)

The theoretical detention time of water is

$$T = \frac{V}{Q} \quad (10)$$

where
Q = discharge of the outlet ($L^3$ $T^{-1}$)

The theoretical detention time of the substance is defined analogically, with the difference that the input but not the output is included in the equation:

$$T_m = \frac{m}{I} \quad (11)$$

where
$T_m$ = theoretical detention time of the substance (T)

$T_m$ expresses the average time that a molecule of the substance considered will be in the lake (or the water body) after being discharged into it.

In the following sections the mathematical definitions for the parameters in different descriptions will be given. The retention will be expressed either as a first order or a second order net reaction. For all the modifications both **voluminal** and **areal** versions can be applied. In voluminal modifications the retention is assumed to be proportional to concentration, as in the traditional model of Vollenweider (1969), or the square of concentration, and to the volume of the water body. In areal modifications the area of the lake or sub-basin is used instead of volume (e.g. Chapra 1975). The relationship between voluminal and areal sedimentation coefficients is thus:

$$k = \frac{k_a}{\bar{z}} \quad (12)$$

where
$\bar{z}$ = average depth (= V/A) (L)
$k_a$ = areal sedimentation coefficient
k = voluminal sedimentation coefficient

The dimensions of $k_a$ and k depend on the order of the reaction kinetics.

Table 1. The different modifications of the model development. The codes given in this table will be used later. Both voluminal and areal versions of each modification will be considered, but the distinction has not been made in this table.

| Hydraulic description | Order of the loss kinetics | |
|---|---|---|
| | First order | Second order |
| CSTR | CSTR, first order (C1) | CSTR, second order (C2) |
| PFR | PFR with no additional input, first order (PN1) | PFR with no additional input, second order (PN2) |
| | PFR with additional input, first order (PA1) | PFR with additional input, second order (PA2) |
| Combination of PFR and CSTR | Combination of PFR and CSTR with no additional input, first order (PCN1) | Combination of PFR and CSTR with no additional input, second order (PCN2) |
| | Combination of PFR and CSTR with additional input, first order (PCA1) | Combination of PFR and CSTR with additional input, second order (PCA2) |

The corresponding conservative equations are easily obtained on the basis of the corresponding models with first order retention kinetics when the value of zero is given to the reaction coefficient. However, in some cases the reaction coefficient is in the denominator of the formula and another formulation must then be applied in order to get a correct mass balance description for a conservative substance.

The hydraulic description of the continuously stirred tank reactor (CSTR), two versions of the plug flow reactor (PFR) as well as two versions of a linear combination of PFR and CSTR have been chosen (Table 1). Both voluminal and areal modifications have been considered. For each model version the basic mass balance equation and the formulae (or methods) for calculating the following quantities are presented: steady state concentration, reaction coefficient, retention, retention coefficient, total mass and the detention time of the substance.

## 3.2 CSTR models

### 3.2.1 General

The principles of **continuously stirred tank reactor** (CSTR) lake models were thoroughly studied by Vollenweider (1969, 1975). Although

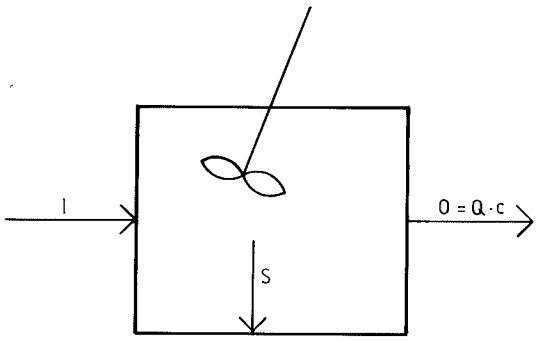



Fig. 3. The schematic presentation of CSTR. I = input, O = output, Q = discharge, c = concentration, S = effect of the internal processes.

continuously stirred tank reactor is only a rough simplification of the behaviour of a lake it is one of the most applicable descriptions of dimictic lakes if long-term averages are considered. In the CSTR description the input of the substance is assumed to mix immediately, the concentration is assumed to be uniform throughout the lake and therefore the concentration at the outlet must be equal to the (average) concentration in the lake (Fig. 3).

### 3.2.2 First order kinetics (C1)

The retention of the substance is here considered as a first order reaction. The steady-state mass balance equation in this case can be written as follows (see Fig. 3):

$$\frac{dc}{dt} = \frac{I}{V} - \frac{Q}{V}c - k\,c = 0 \qquad (13)$$

where

k = first order (voluminal) reaction coefficient ($T^{-1}$)

Equation (13) represents the voluminal version, where retention is assumed to be proportional to concentration and volume (Vollenweider 1969). The corresponding areal version (Chapra 1975) is easily obtained by substituting $k_a/\bar{z}$ for k, where $k_a$ = first order areal reaction coefficient and $\bar{z}$ = average depth (Eq. 12). The dimension of the first order areal coefficient is thus $L\,T^{-1}$. The explicit forms of the equations for the areal versions, which can be written taking into account the fact that the average depth is volume/area, are not, however, presented because they are practically similar to the voluminal equations.

The steady-state concentration is obtained from Eq. (14):

$$c = \frac{I}{Q + kV} \qquad (14)$$

For applications of this kind of models it is important to know the values of the reaction coefficients. For this case the reaction coefficient can be calculated on the basis of observational data using the following equation:

$$k = \frac{I - Qc}{cV} \qquad (15)$$

The retention of the substance, as defined by Eq. (7), is calculated as follows:

$$S_{ret} = \frac{kIV}{Q + kV} \qquad (16)$$

Thus the retention coefficient (Eq. 9) is

$$R = \frac{kV}{Q + kV} = \frac{k}{\rho + k} \qquad (17)$$

where

$\rho$ = water renewal coefficient or flushing coefficient ($T^{-1}$), the inverse value of the theoretical detention time T

The total amount of the substance considered, expressed as a function of the basic variables (I, V, Q, k), is as follows:

$$m = \frac{IV}{Q + kV} \qquad (18)$$

and the detention time of the substance as follows:

$$T_m = \frac{V}{Q + kV} = \frac{T}{1 + kT} \qquad (19)$$

### 3.2.3 Second order kinetics (C2)

The idea of applying second order retention kinetics was originally based on the retention models of Lappalainen (1974, 1975a, b, 1977) and has been further applied in several studies (see e.g. Eloranta et al. 1981, Frisk 1981a, see also Section 2.4). The modification presented here was been presented earlier by Frisk (1983).

The basic equation is as follows (see Fig. 3):

$$\frac{dc}{dt} = \frac{I}{V} - \frac{Q}{V}c - ac^2 = 0 \qquad (20)$$

where
a = second order (voluminal) reaction coefficient ($(M\,L^{-3})^{-1}\,T^{-1}$)

The corresponding areal equation is obtained by substituting the ratio $a_a/\bar{z}$ (where $a_a$ = second order areal reaction coefficient and $\bar{z}$ = average depth) for the coefficient a. The dimension of $a_a$ is $(M\,L^{-4})^{-1}\,T^{-1}$.

The solution of Eq. (20) is:

$$c = \frac{1}{2a}\left(-\frac{1}{T} + \sqrt{\left(\frac{1}{T}\right)^2 + 4a\frac{I}{V}}\right) \qquad (21)$$

If a = 0 concentration is equal to the mixing concentration (=I/Q). The reaction coefficient can be calculated using Eq. (22):

$$a = \frac{I - Qc}{c^2 V} \qquad (22)$$

where
c = average concentration in the lake ($M\,L^{-3}$)

In the calculation of the retention the following equation is used:

$$S_{ret} = \frac{1}{2a}\left(\frac{Q}{T} + 2aI - Q\sqrt{\left(\frac{I}{T}\right)^2 + 4a\frac{I}{V}}\right) \qquad (23)$$

The retention coefficient can be expressed as follows:

$$R = \frac{1}{2a}\left(\frac{\rho}{c_I} + 2a - \frac{1}{c_I}\sqrt{\left(\frac{I}{V}\right)^2 + 4a\frac{I}{V}}\right) \qquad (24)$$

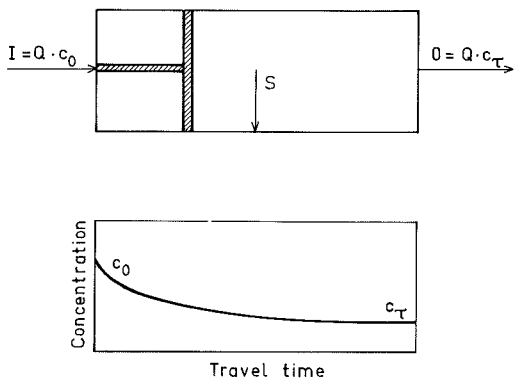



Fig. 4. The schematic presentation of PFR with no additional input. I = input, Q discharge, $c_0$ = concentration at travel time $\tau$ = 0, $c_\tau$ = concentration at travel time $\tau$, S = effect of the internal processes.

where
$c_I = I/Q$ ($M\,L^{-3}$)

The expression for the total amount of the substance is:

$$m = -\frac{1}{2a}\left(Q - \sqrt{Q^2 + 4aIV}\right) \qquad (25)$$

and for the detention time of the substance:

$$T_m = \frac{1}{2aI}\left(Q - \sqrt{Q^2 + 4aIV}\right) \qquad (26)$$

## 3.3 PFR models with no additional input

### 3.3.1 General

The idea of a **plug flow reactor** (PFR) is totally opposed to that of a completely stirred tank reactor. No mixing is assumed to occur in the longitudinal direction. This kind of approach has traditionally (since the days of Streeter and Phelps) been applied to rivers. The application of PFR to river-run lakes has also proved to be possible, and plug flow hydraulics have been applied to elongated lakes with long detention times (e.g. Granberg and Harjula 1981). The graphical presentation of PFR is in Fig 4.

### 3.3.2 First order kinetics (PN1)

The basic equation is similar to the Streeter-Phelps equation for BOD decay:

$$\frac{dc}{d\tau} = -kc \qquad (27)$$

where
$\tau$ = travel time (= detention time) (T)
k = first order (voluminal) reaction coefficient ($T^{-1}$)

The corresponding areal model is obtained by substitution of $k_a/\bar{z}$ for k, where $k_a$ = first order areal reaction coefficient ($L\,T^{-1}$) and $\bar{z}$ = average depth (L).

Integration of Eq. (27) yields

$$c_\tau = c_0\, e^{-k\tau} \qquad (28)$$

where
$c_\tau$ = concentration at travel time $\tau$ ($M\,T^{-1}$)
$c_0$ = concentration at travel time 0 ($M\,T^{-1}$)

The reaction coefficient can be calculated as follows:

$$k = \frac{1}{\tau} \ln \frac{c_0}{c_\tau} \tag{29}$$

If a normal river-run lake is considered the travel time ($\tau$) can be estimated using the theoretical detention time of the lake T (=V/Q).

For calculating the retention Eqs. (7) and (28) are applied:

$$S_{ret} = Q\, c_0\, (1 - e^{-kT}) \tag{30}$$

The retention coefficient is, of course,

$$R = 1 - e^{-kT} \tag{31}$$

In order to calculate the total amount of the substance, integration is necessary:

$$m = \int_0^V c_\tau \, dV \tag{32}$$

where
$dV = A_x\, dx$ ($L^3$)
$A_x$ = cross-sectional area ($L^2$)
$dx$ = differential of the distance coordinate (L)

The connections

$$dx = \bar{u}\, d\tau \tag{33}$$

where
$\bar{u}$ = average velocity of flow ($L\, T^{-1}$)
and

$$Q = A_x\, \bar{u} \tag{34}$$

must be taken into account. On the basis of Eqs. (28), (32), (33) and (34) Eq. (35) can be written:

$$m = \frac{Q\, c_0}{k} (1 - e^{-kT}) \tag{35}$$

The detention time of the substance is:

$$T_m = \frac{1 - e^{-kT}}{k} \tag{36}$$

### 3.3.3 Second order kinetics (PN2)

This modification will be presented analogically to the first order modification. A second order plug flow model similar to the one presented here was proposed by Frisk (1981a, 1983). In Frisk's (1981a) studies it appeared that the sedimentation exponent for phosphorus should be 1.9 rather than 2.

The basic equation is

$$\frac{dc}{d\tau} = -\, a c^2 \tag{37}$$

where
a = second order (voluminal) reaction coefficient ($M^{-1}\, L^3\, T^{-1}$)

The solution is

$$c_\tau = \frac{c_0}{1 + \tau a c_0} \tag{38}$$

where
$c_\tau$ = concentration at travel time ($M\, L^{-3}$)
$c_0$ = concentration at the beginning of the lake basin ($M\, L^{-3}$)
and the formula for calculating the reaction coefficient on the basis of empirical data

$$a = \frac{c_0 - c_\tau}{c_\tau\, c_0\, \tau} \tag{39}$$

The corresponding areal version is obtained as in connection with Eq. (20). The retention can be calculated as follows:

$$S_{ret} = Q \frac{T\, a\, c_0^2}{1 + T\, a\, c_0} \tag{40}$$

The retention coefficient is thus

$$R = \frac{T\, a\, c_0}{1 + T\, a\, c_0} \tag{41}$$

The total amount of the substance can be calculated as follows:

$$m = \int_0^V c_\tau \, dV = \int_0^T c_\tau\, A_x\, \bar{u}\, d\tau = Q \int_0^T \frac{c_0}{1 + \tau\, a\, c_0}\, d\tau =$$

$$\frac{Q}{a} \int_0^T \frac{a c_0}{1 + \tau\, a\, c_0}\, d\tau = \frac{Q}{a} \ln (1 + a\, T\, c_0) \tag{42}$$

The detention time of the substance is:

$$T_m = \frac{\ln (1 + a\, c_0\, T)}{a\, c_0} \tag{43}$$

## 3.4 PFR models with additional input

### 3.4.1 General

The problem with PN1 and PN2 models is that additional input (e.g. diffuse loading) cannot be taken into account in a suitable way. If the additional input can be assumed to be constant, the models of the previous sections can be modified to yield a more realistic description. The graphical presentation of this kind of models can be seen in Fig. 5.

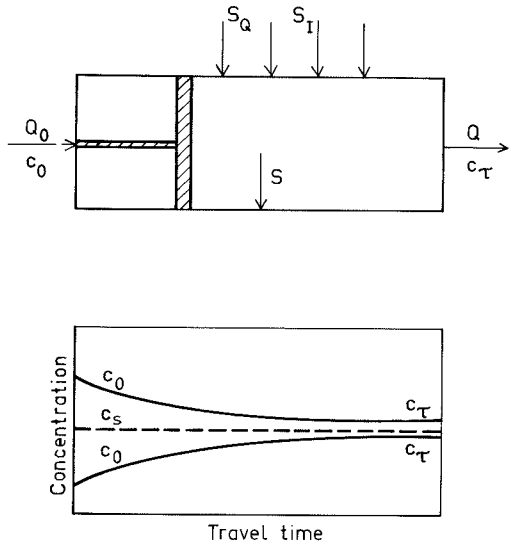



Fig. 5. The schematic prsentation of PFR with additional input. $Q_0$ = initial discharge, $S_Q$ = additional input of water, $Q_\tau$ = discharge at travel time $\tau$, $S_I$ = additional input of the substance considered, $c_0$ = concentration at travel time $\tau = 0$, $c_\tau$ = concentration at travel time $\tau$, $c_S$ = equilibrium concentration ($\tau = \infty$), S = effect of the internal processes.

### 3.4.2 First order kinetics (PA1)

The basic equation, which is similar in principle to the BOD model of Li (1962), is

$$\frac{dc}{d\tau} = \frac{S_I}{A_X} - \frac{S_Q}{A_X} c - kc \qquad (44)$$

where
$S_I$ = additional input of the substance considered ($M\ T^{-1}\ L^{-1}$)
$S_Q$ = additional input of water ($L^3\ T^{-1}\ L^{-1}$)
k = first order (voluminal) reaction coefficient ($T^{-1}$)

The corresponding areal model is obtained exactly in the same way as in connection with the PN1 model. Equation (44) with constant values of $S_I$ and $S_Q$ can easily be solved by integration using the initial condition $c = c_0$ when $\tau = 0$:

$$c_\tau = c_0\, e^{-K_e \tau} + c_s\,(1 - e^{-K_e \tau}) \qquad (45)$$

where
$c_\tau$ = concentration at travel time $\tau$ ($M\ L^{-3}$)

$$c_s = \frac{S_I}{S_Q + k A_X}$$

$$K_e = k + \frac{S_Q}{A_X}$$

The first order reaction coefficient can be calculated as follows:

$$k = \frac{1}{\tau} \ln\left(\frac{c_0 - c_s}{c_\tau - c_s}\right) - \frac{S_Q}{A_X} \qquad (46)$$

The condition for the solution presented in Eq. (45) is that $S_I$, $S_Q$ and $A_X$ are constant. If this kind of assumption is made it is most logical to use a special kind of hydraulic description presented by Frisk (1984). The discharge at different points is calculated using Eq. (47):

$$Q_x = Q_0 + S_Q\, x \qquad (47)$$

where
x = distance from the beginning of the lake or the sub-basin (L)
$Q_x$ = discharge at distance x ($L^3\ T^{-1}$)

The discharge at the outlet of the lake (or the sub-basin) is thus

$$Q_T = Q_0 + \frac{V}{A_x} S_Q \qquad (48)$$

where
$Q_T$ = discharge at the outlet of the lake or the sub-basin ($L^3\ T^{-1}$)

Because $A_x$ is constant but discharge increases according to Eq. (47) the average velocity of flow increases:

$$\bar{u}(x) = \frac{Q_0}{A_x} + \frac{S_Q}{A_x} x \qquad (49)$$

where
$\bar{u}(x)$ = average velocity of flow at distance x ($L\ T^{-1}$)

The detention time of water is then obtained by integration:

$$\tau(x) = \int_0^x \frac{dx}{\bar{u}(x)} = \frac{A_x}{S_Q}(\ln(1 + \frac{S_Q}{Q_0} x) \quad (50)$$

where
$\tau(x)$ = detention time at distance x (T)

The detention time of the whole lake (or the sub-basin) is thus

$$T = \frac{A_x}{S_Q}(\ln(1 + \frac{S_Q}{Q_0}\frac{V}{A_x})) \quad (51)$$

The total input is

$$I = Q_0 c_0 + S_I \frac{V}{A_x} \quad (52)$$

The retention of the substance in the system is

$$S_{ret} = I - Q_T c_T \quad (53)$$

where I is calculated using Eq. (52), $c_T$ (= the concentration at the outlet of the lake or the sub-basin) using Eq. (45) with travel time $\tau = T$, i.e. the detention time of the whole lake, and $Q_T$ using Eq. (48). By definition the retention coefficient is obtained from Eqs. (52) and (53) as the ratio of retention and total input.

The total amount of the substance is calculated as follows:

$$m = \int_0^V c_\tau \, dV \quad (54)$$

where
$c_\tau$ = concentration computed by Eq. (45) (M $L^{-3}$)
$dV = A_x \, dx$

The differential of x can be calculated using Eq. (50):

$$dx = \frac{Q_0}{A_x} e^{\frac{S_Q}{A_x}\tau} d\tau \quad (55)$$

On the basis of Eqs. (54) and (55) total mass can be calculated:

$$m = \frac{Q_0}{k}(c_s - c_0)\left[\left(\frac{Q_T}{Q_0}\right)^{-k\frac{A_x}{S_Q}} - 1\right] + c_s V \quad (56)$$

The detention time of the substance is calculated by dividing total mass by total input, although the conceptual meaning of $T_m$ is here different, because the detention time of a single molecule depends on the place where it was discharged to the system:

$$T_m = \frac{m}{Q_0 c_0 + S_I V/A_x} \quad (57)$$

where m = mass calculated by Eq. (56)

### 3.4.3 Second order kinetics (PA2)

The basic model was presented with the name of JOP (a phosphorus model for rivers) by Frisk (1984). The model has been applied e.g. to the rivers Kiiminkijoki (Saari 1986) and Ounasjoki (Itkonen and Kinnunen 1986). The mass balance equation is the following:

$$\frac{dc}{d\tau} = \frac{S_I}{A_x} - \frac{S_Q}{A_x} c - a c^2 \quad (58)$$

Eq. (58) is the voluminal version and the areal version is obtained as in connection with Eq. (20). Equation (58) can easily be solved analytically if $S_I$, $S_Q$ and $A_x$ are constant (Frisk 1984). There are different solutions for Eq. (58) depending on whether the concentration is greater or smaller than or as great as the equilibrium concentration (which will be defined later).

For solving Eq. (58) the derivative of the left-hand side is set as zero and the roots of the second degree equation are the following:

$$r_1 = -\frac{1}{2a}\left(\frac{S_Q}{A_x} + \sqrt{\left(\frac{S_Q}{A_x}\right)^2 + 4a\frac{S_I}{A_x}}\right) \quad (59)$$

$$r_2 = -\frac{1}{2a}\left(\frac{S_Q}{A_x} - \sqrt{\left(\frac{S_Q}{A_x}\right)^2 + 4a\frac{S_I}{A_x}}\right) \quad (60)$$

Because $r_1$ is always negative $r_2$ represents the equilibrium concentration that would be achieved if the travel time were eternally long. If the initial concentration $c_0$ is the same as $r_2$ the concentration remains constant in the whole system.

If $c_0 > r_2$ the solution is the following:

$$c_\tau = \frac{r_1(c_0 - r_2) - r_2(c_0 - r_1)\, e^{-(r_1 - r_2)\, a\, \tau}}{(c_0 - r_2) - (c_0 - r_1)\, e^{-(r_1 - r_2)\, a\, \tau}} \quad (61)$$

If $c_0 < r_2$ the solution is the following:

$$c_\tau = \frac{r_1(r_2 - c_0) + r_2(c_0 - r_1)\, e^{-(r_1 - r_2)\, a\, \tau}}{(r_2 - c_0) + (c_0 - r_1)\, e^{-(r_1 - r_2)\, a\, \tau}} \quad (62)$$

Because $r_1$ and $r_2$ are dependent on the second order reaction coefficient (a) it is not possible to get an analytical solution for the coefficient a but it must be solved by iteration.

The hydraulic description is the same as in the first order model (PA1) and so Eqs. (47)—(52) are also valid here.

The retention of the substance can be calculated using Eq. (63)

$$S_{ret} = Q_0\, c_0 + S_I \frac{V}{A_x} - Q_T\, c_T \quad (63)$$

where

$c_T$ = concentration at the outlet of the sub-basin, in Eq. (61) or (62) $\tau = T$

$Q_T$ = discharge at the outlet of the sub-basin, Eq. (48)

and the retention coefficient using Eq. (64)

$$R = \frac{S_{ret}}{I} \quad (64)$$

where

$S_{ret}$ = retention calculated using Eq. (63)

$I$ = total input calculated using Eq. (52)

The total mass is calculated as in the case of the first order model (PA1):

$$m = Q_0 \int_0^T c_\tau\, e^{\frac{S_Q}{A_x}\tau}\, d\tau \quad (65)$$

where

$c_\tau$ = concentration calculated using Eq. (61) or (62)

$T$ = detention time calculated using Eq. (51)

Numerical integration must be used. The detention time of the substance is calculated using Eq. (57) with the difference that m must be calculated using Eq. (65).

## 3.5 Combination of PFR and CSTR, with no additional input

### 3.5.1 General

The CSTR and PFR models presented in the previous sections represent totally opposite situations. In PFR no mixing in the longitudinal direction is assumed to occur at all. In reality many lakes, especially the so-called river-run lakes (Chapra and Reckhow 1983), are partially mixed. The most common way of describing partial mixing is to use an advection-dispersion equation that is a second order partial differential equation but which reduces to an ordinary differential equation at steady state. Analytical solutions for different modifications of this kind of equations have been presented e.g. by van Genuchten and Alves (1982).

Chapra and Reckhow (1983) presented a first order retention model for river-run lakes. They also presented the methodology of how to consider many successive sub-basins. However, if additional input along the sub-basin is allowed or second order kinetics are employed, difficulties arise in finding analytical solutions.

An alternative way of taking into account partial mixing was chosen in this study. It is based on a combination of the PFR and CSTR descriptions. This kind of approach has been used e.g. by Perttunen and Alasaarela (1981) in the oxygen model originally developed for the reservoir of Uljua. Although this approach does not give as realistic descriptions of the spatial distribution of the advection-dispersion equation it provides simple and easily applicable models in which the degree of mixing can be regulated.

The basic equation can be written as follows:

$$c = D c_p + (1 - D) c_c \quad (66)$$

where

$D$ = plug flow coefficient (dimensionless)

$c_p$ = concentration calculated using the plug flow equation ($M\, L^{-3}$)

$c_c$ = concentration calculated using the CSTR equation ($M\, L^{-3}$)

The coefficient D expresses the extent to which the lake behaves like a plug flow reactor. The CSTR and PFR concentrations are calculated using equations presented in Sections 3.2 and 3.3, respectively. It may be easier to imagine this kind of system if we think that part of the volume and correspondingly part of the discharge is in plug flow and part is completely mixed (the share is expressed by the coefficient D). Thus the detention time for both terms is the same as for the whole lake (Fig. 6).

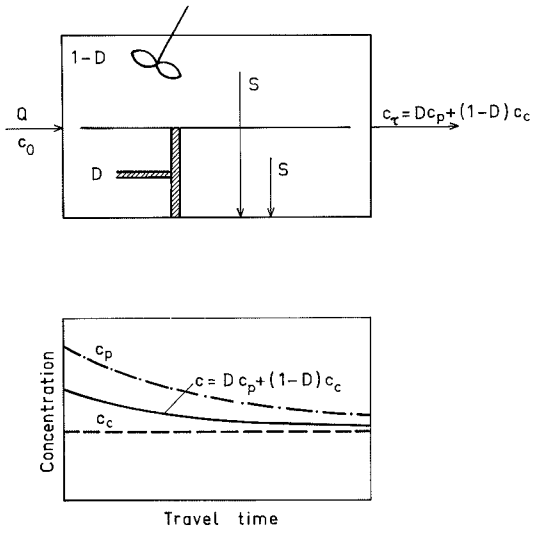



Fig. 6. Schematic presentation of the combination of PFR and CSTR with no additional input. Q = discharge, $c_0$ = concentration at travel time $\tau = 0$, $c_p$ = PFR concentration, $c_c$ = CSTR concentration, $c_\tau$ = concentration at travel time $\tau$, D = plug flow coefficient, S = effect of the internal processes.

### 3.5.2 First order kinetics (PCN1)

According to Eq. (14)

$$c_c = \frac{c_0}{1+kT} \tag{67}$$

where
$c_0$ = mixing concentration = I/Q (M $L^{-3}$)
T = theoretical detention time = V/Q (T)

and according to Eq. (27)

$$c_{p\tau} = c_0\, e^{-k\tau} \tag{68}$$

where
$\tau$ = travel time (= detention time) (T)
$c_{p\tau}$ = concentration at travel time $\tau$ calculated using the plug flow equation

$$c_{p\tau} = c_0\, e^{-k\tau} \tag{69}$$

Eq. (66) can thus be written in the form

$$c_\tau = c_0\,(D\, e^{-k\tau} + (1-D)\frac{1}{1+kT}) \tag{70}$$

and for the whole lake or the sub-basin considered

$$c_T = c_0\,(D\, e^{-kT} + (1-D)\frac{1}{1+kT}) \tag{71}$$

If D = 1 Eqs. (70) and (71) reduce to the ordinary plug flow model and if D = 0 to the CSTR model.

The kinetic coefficient k cannot be solved analytically but its value must be sought by iteration.

Retention of the substance is calculated using Eq. (72):

$$S_{ret} = Q\, c_0\,(1 - \frac{1-D}{1+kT} - D\, e^{-kT}) \tag{72}$$

and the retention coefficient using Eq. (73):

$$R = 1 - \frac{1-D}{1+kT} - D\, e^{-kT} \tag{73}$$

The total amount of the substance is the sum of the PFR and CSTR terms. On the basis of Eqs. (18), (35) and (66)

$$m = c_0\,(\frac{(1-D)V}{1+kT} + \frac{DQ}{k}(1 - e^{-kT})) \tag{74}$$

The detention time of the mass is correspondingly

$$T_m = \frac{(1-D)T}{1+kT} + \frac{D}{k}(1 - e^{-kT}) \tag{75}$$

### 3.5.3 Second order kinetics (PCN2)

The basic equation (66) is also applied here. The PFR and CSTR concentrations are calculated using Eqs. (38) and (21), respectively, and their combination produces Eq. (76):

$$c_\tau = \frac{Dc_0}{1+ac_0\tau} + \frac{1-D}{2a}(-\rho + \sqrt{\rho^2 + 4a\frac{I}{V}}\,) \tag{76}$$

Here again a value of 1 for D produces plug flow and the value 0 complete mixing. The coefficient a must be calculated by iteration.

The equation for retention is:

$$S_{ret} = Qc_0\,(1 - \frac{D}{1+ac_0T} - \frac{1-D}{2ac_0}(-\rho + \sqrt{\rho^2 + 4ac_0\rho}\,)) \tag{77}$$

and for the retention coefficient:

$$R = 1 - \frac{D}{1+ac_0T} - \frac{1-D}{2ac_0}(-\rho + \sqrt{\rho^2 + 4ac_0\rho}\,) \tag{78}$$

In calculating total mass Eqs. (42) and (25) can be utilized:

$$m = D\frac{Q}{a}(\ln(1+ac_0T) + \frac{1-D}{2a}(-Q+\sqrt{Q^2+4aQc_0V}) \quad (79)$$

The detention time of mass is then

$$T_m = \frac{D}{ac_0}\ln(1+ac_0T) + \frac{(1-D)T}{2ac_0}(-1+\sqrt{1+4ac_0T}) \quad (80)$$

## 3.6 Combination of PFR and CSTR, with additional input

### 3.6.1 General

It is most logical to assume that additional input is mixed in the same ratio as initial input (Fig. 7). The total input is calculated by Eq. (52) and the total discharge by Eq. (48).

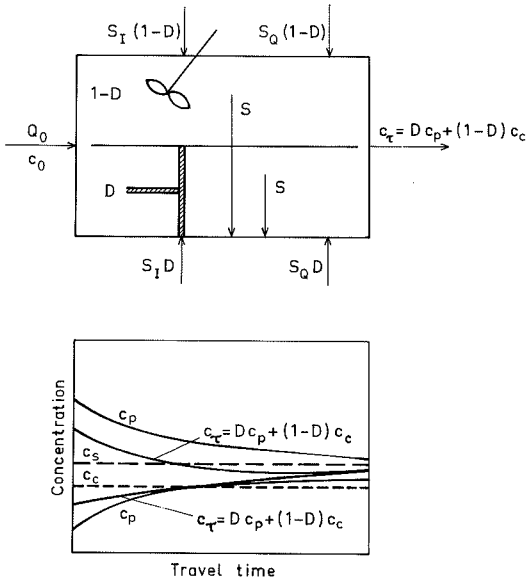



Fig. 7. Schematic presentation of the combination of PFR and CSTR with additional input. $Q_0$ = initial discharge, $S_Q$ = additional input of water, $S_I$ = additional input of the substance concidered, $c_0$ = concentration at travel time $\tau = 0$, $c_p$ = PFR concentration, $c_c$ = CSTR concentration, $c_\tau$ = concentration at travel time $\tau$, $c_s$ = equilibrium concentration ($\tau = \infty$), D = plug flow coefficient, S = effect of the internal processes.

### 3.6.2 First order kinetics (PCA1)

The basic equation is again Eq. (66). The CSTR concentration needed in Eq. (66) is calculated as follows:

$$c_c = \frac{Q_0c_0 + S_IV/A_x}{kV + Q_0 + S_QV/A_x} \quad (81)$$

For the plug flow term the same kind of hydraulic description as in Section 3.4 is applied and Eq. (45) is used. The combination produces

$$c_\tau = D\,(c_0\,e^{-K_e\tau} + c_s\,(1-e^{-K_e\tau})) + (1-D)\frac{Q_0c_0 + S_IV/A_x}{kV + Q_0 + S_QV/A_x} \quad (82)$$

where $c_s = \frac{S_I}{S_Q + kA_x}$

and $K_e = k + \frac{S_Q}{A_x}$

The coefficient k must be calculated by iteration.

The equation for retention can be formed using Eqs. (48), (52) and (53), calculating $c_T$ with Eq. (82) with detention time $\tau = T$ calculated using Eq. (51). The retention coefficient is retention divided by total input calculated with Eq. (52).

Total mass can be calculated in the following way:

$$m = Dm_p + (1-D)Vc_c \quad (83)$$

where
$m_p$ = PFR total mass calculated with Eq. (56)
$c_c$ = CSTR concentration calculated with Eq. (81)

The detention time of mass is correspondingly

$$T = \frac{I}{m} \quad (84)$$

where
m = total mass calculated with Eq. (83)
I = total input calculated Eq. (52)

### 3.6.3 Second order kinetics (PCA2)

The description of the hydraulics is similar to PCA1. The basic Equation (66) is valid here, too. The PFR concentration is calculated using Eqs. (61) and (62). The CSTR concentration is calculated by means of Eq. (21) as follows:

$$c_c = -\frac{1}{2a}\left(\frac{Q_0 + S_Q V/A_x}{V} - \sqrt{\left(\frac{Q_0 + S_Q V/A_x}{V}\right)^2 + 4a\left(\frac{Q_0 c_0 + S_I V/A_x}{V}\right)}\right) \quad (85)$$

Here again the reaction coefficient a must be solved using iteration.

For retention and the retention coefficient the same approach as in Section 3.6.2 can be used with the difference that the first order formulae are replaced by the corresponding second order formulae.

In calculating total mass the basic equation (83) is valid. The CSTR concentration must be calculated with Eq. (85) and the PFR total mass using numerical integration, as explained in Section 3.4.3 (Eq. 65).

The detention time of mass can be calculated as explained in Section 3.6.2.

# 4. MATERIALS AND METHODS

## 4.1 The lake data

### 4.1.1 General

The different model modifications were tested against empirical data of two lakes, Lake Haukivesi and Lake Päijänne, both situated in central of Finland. Like many Finnish lakes, the lakes are elongated and cannot be considered as homogenous water bodies, but the areal distribution of water quality must be taken into account. For this purpose the lakes have been divided into sub-basins in mass balance studies. One reason for the choice of lakes Haukivesi and Päijänne was in fact their shape. It is possible to test model modifications with different hydraulic descriptions in this kind of lake systems. The main emphasis was on the consideration of the different modifications, for the general validity of the models cannot be tested using data of only two lakes.

The data of Lake Haukivesi and Lake Päijänne are presented in Sections 4.1.2 and 4.1.3, respectively. In Section 4.2 the methods used in testing the models are described.

### 4.1.2 Lake Haukivesi

Lake Haukivesi (meaning in English **pike lake**) is situated in central Finland between the towns of Varkaus and Savonlinna. It is a part of Lake Suur-Saimaa, the largest lake in Finland (Fig. 8). The surface area of Lake Haukivesi is 514 $km^2$, its greatest length about 80 km and its volume $4\,660 \cdot 10^6$ $m^3$ (Kauppi et al. 1985). The lake is dominated by islands and bays, but the general impression is that the lake is a rather narrow, elongated lake. Its orientation is from north-west to south-east, as in the case of most lakes in inland parts of Finland due to the effects of the last glacial period. The drainage area of Lake Haukivesi is 9 410 $km^2$ and the lake percentage of the drainage basin is 27.3 % (Seuna 1971).

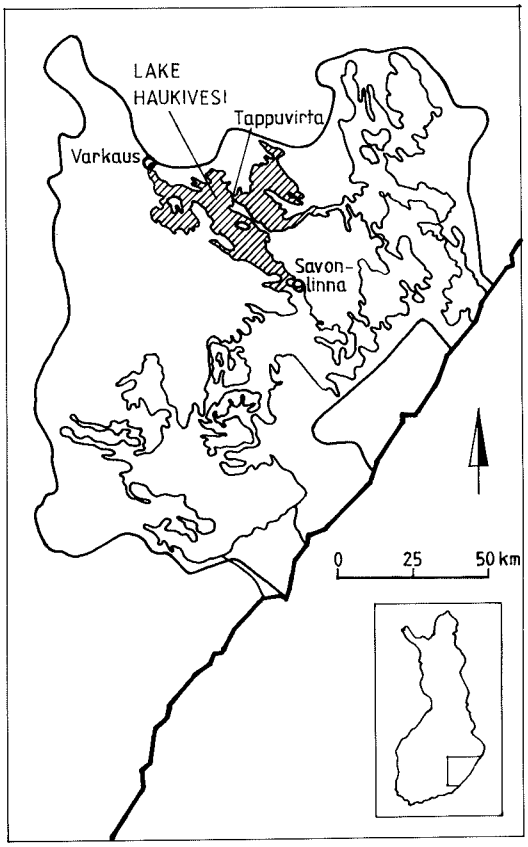



Fig. 8. Lake Haukivesi as a part of Lake Suur-Saimaa.

Lake Haukivesi is loaded by effluents of the wood-processing industry (Enso-Gutzeit Oy, until March 1987 A. Ahlström Oy) and of the town of Varkaus. Major changes were carried out in the factories of A. Ahlström Oy in 1977—1980. A sulphate process was substituted for the earlier sulphite process and a mechanical-biological waste water treatment plant was taken into use. The

treatment plant has considerably reduced the BOD loading but increased nitrogen loading. Increase in phosphorus loading during the 1980s was caused by the increase in pulp and paper production.

Other loading sources of Lake Haukivesi are minor. According to Kauppi et al. (1985) the share of cultivated fields in the nearest drainage area is about 7 %. Application of the the formulae of Kauppi (1978) leads to the conclusion that the diffuse loading caused by agriculture is not an important eutrophicating factor.

Several studies have been carried out on Lake Haukivesi (e.g. Lappalainen 1968, 1974, Aaltonen 1978, 1981, Mankki 1980, Frisk 1981b, Hakkari and Lappalainen 1981, Matinvesi 1984, Panula-Ontto-Suuronen 1987). Lappalainen (1974, 1975a, b) developed a predictive model for hypolimnetic dissolved oxygen concentration, in which both primary and secondary oxygen consumption was included. Secondary oxygen consumption, due to decomposition of autochtonous organic matter, was calculated as a function of phosphorus loading and hydrological and morphometric data.

In this study, like in corresponding earlier modelling studies (Lappalainen 1974, Frisk 1981a, b, Panula-Ontto-Suuronen 1987), only the main stream area of Lake Haukivesi was considered and the bays and other shallow areas outside the main stream area were excluded. Correspondingly, the effective volumes of the different sub-basins were used. The eastern part of the lake, i.e. the area east of Tappuvirta (Figs. 8 and 9) was excluded from the study area.

Frisk (1981b) found an inconsistency in the loading, discharge and water quality data in the northernmost part of Lake Haukivesi. The high phosphorus concentrations of the lake could not be explained by phosphorus loadings and the input from the upper watercourse, even when release from the sediment was taken into account. Possible explanations for the "missing" part of the loading have been proposed to be storage of the timber in

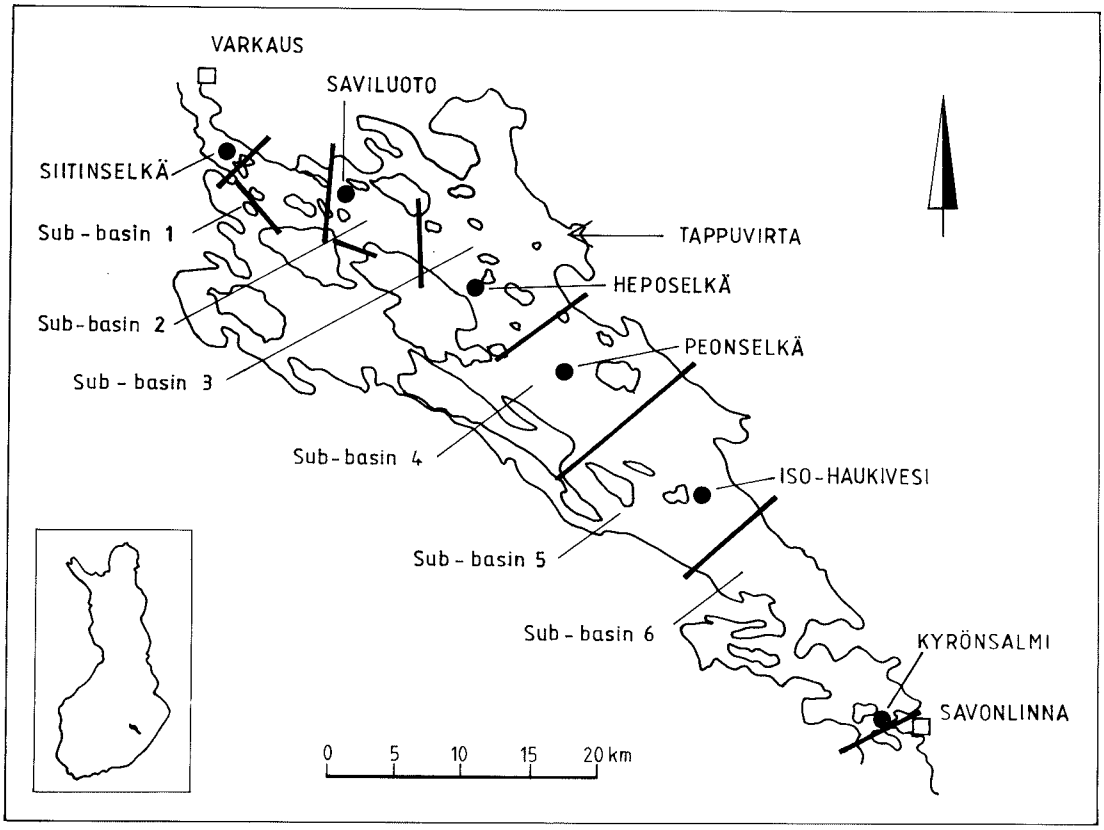



Fig. 9. The sub-basins and the sampling points of Lake Haukivesi, used in this study.

the Huruslahti bay in Varkaus (Savolainen 1984) and exceptionally high release of phosphorus from the sediment in the northernmost part of the lake.

Because of this inconsistency and because the purpose of this study was not to describe the effects of industrial and domestic effluents on the state of Lake Haukivesi, the northernmost sub-basin (Siitinselkä) used in the studies of Lappalainen (1974), Frisk (1981b) and Panula-Ontto-Suuronen (1987) was excluded. The measured concentrations of the sampling point of Siitinselkä (Fig. 9) were used as input data for phosphorus concentration at the inlet of the application area of the models (Fig. 10). The sampling points and sub-basins of this study have been presented in Fig. 9 and the model system layout of Lake Haukivesi in Fig. 10.

As described in Section 3, the data needed for testing the models consist of hydrological (discharges) and morphometric data (volumes, areas and lengths of the sub-basins, locations of the sampling points) and data on phosphorus inputs and concentrations in the water body. Data of the years 1976—1985 were used. In mass balance studies a ten-year period can be considered very satisfactory.

The input discharge values were calculated on the basis of the data obtained from the Hydrological Office of the National Board of Waters and the Environment, taking advantage of the data on the drainage areas (Seuna 1971) and measured discharge values. The effect of precipitation and evaporation on the water balance was estimated on the basis of the reports for Lake Päijänne (see Section 4.1.3).

The effective volumes (Table 2) of the sub-basins were calculated on the basis of data obtained from the Water and Environment District of Kuopio (sub-basins 1—3) and taken from the study of Lappalainen (1974) (sub-basins 4—6). The lengths

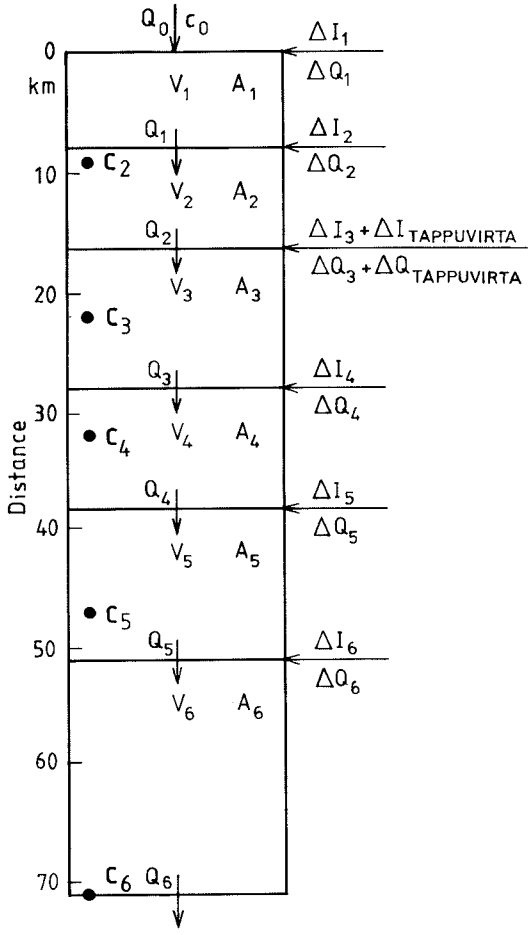



Fig. 10. The system layout of Lake Haukivesi. $c_0$ = phosphorus concentration of the incoming water, on the basis of measurements at the sampling point of Siitinselkä, $\Delta Q_i$ = additional flow, $\Delta I_i$ = additional input, $V_i$ = volume, $c_i$ = concentration. $V_i$ values have been presented in Table 2 and $c_0$, $Q_0$, $c_i$, $\Delta Q_i$ and $\Delta I_i$ values in Appendix 1.

Table 2. Morphometric data of the sub-basins of Lake Haukivesi (Fig. 10). The location of the sampling points is expressed in kilometers downstream from the beginning of the sub-basin. The sampling point of Siitinselkä is assumed to represent the input concentration of sub-basin 1, although in reality it is situated slightly upstream from the beginning of sub-basin 1.

| Sub-basin number | Effective volume $10^6$ m$^3$ | Effective area km$^2$ | Length km | Sampling point | Location of the sampling point, km |
|---|---|---|---|---|---|
| 1 | 103.1 | 19.2 | 8 | Siitinselkä | 0 |
| 2 | 257.1 | 21.3 | 8 | Saviluoto | 1 |
| 3 | 609.2 | 47.5 | 12 | Heposelkä | 6 |
| 4 | 924.0 | 84.0 | 10 | Peonselkä | 4 |
| 5 | 1350.0 | 90.0 | 13 | Iso-Haukivesi | 9 |
| 6 | 858.0 | 78.0 | 20 | Kyrönsalmi | 20 |

of sub-basins and the locations of the sampling points were assessed using maps (Table 2).

The concentration values were obtained from the water quality data bank of the National Board of Waters and the Environment. Two types of concentration data are needed: concentrations for calculating input from rivers and concentrations in the water body, used in the comparison between the observed and calculated values. The inputs from the rivers, which with the exception of Tappuvirta were not very significant, were treated as additional inputs ($\Delta I_i$). Two concentration values of Tappuvirta had to be excluded from the data because they were considered to be false on the basis of mass balances and corresponding lake measurements. However, the conclusion was drawn that more attention should be paid to measurement of the material input from Tappuvirta if the material balances of Lake Haukivesi are to be studied exactly.

In calculating the mean values of total phosphorus concentration in the sampling points of Lake Haukivesi both time and volume weightings were used. In volume weighting the samples of the bottom-nearest water layer were neglected, because the mean values of the water body used in the model represent the mass flow concentrations and phosphorus in the bottom-nearest layer has in effect already been sedimentated. Furthermore, due to the small volume shares the effects of these concentrations are not great. The concentration values of the lake sampling points have been presented in Appendix 1.

The phosphorus inputs coming from the nearest drainage area and from precipitation have little effect on the phosphorus balance of Lake Haukivesi. The input from precipitation was estimated on the basis of the study of Järvinen (1986) and the input from the nearest drainage area was calculated taking advantage of the study of Kauppi (1978). The $\Delta I_i$ values representing the sums of the effects of precipitation, nearest drainage area and rivers flowing to each sub-basin have been presented in Appendix 1. In the preparation of the input data the studies of Frisk (1981b) and Panula-Ontto-Suuronen (1987) were partly utilized.

### 4.1.3 Lake Päijänne

Lake Päijänne is also situated in central Finland. It is the second largest lake in Finland. Its surface area is 1090 km$^2$, the greatest length about 120 km and the volume 17 900 · 10$^6$ m$^3$ (Järvi 1953, Simojoki 1960, Tuunainen et al. 1971). The lake is elongated but has many bays that do not take part in the effective change of water. The lake is oriented from north to south (Fig. 11). The drainage area of Lake Päijänne is 5 575 km$^2$ and the lake percentage of the drainage basin of he lake is 27.2 % (Seuna 1971).

The protection of Lake Päijänne is extremely important. Since the early 1980s the city of Helsinki and neighbouring municipalities have used the lake as a source of raw water (via the Päijänne tunnel).

Lake Päijänne is loaded by the effluents of wood-processing industry situated in Äänekoski and Jämsänkoski. The waste waters of the Äänekoski factories (Metsä-Botnia Oy, until 1982 Metsäliiton Teollisuus Oy) flow to Lake Päijänne through Haapakoski and the waste waters of the Jämsänkoski factories (Yhtyneet Paperitehtaat Oy)

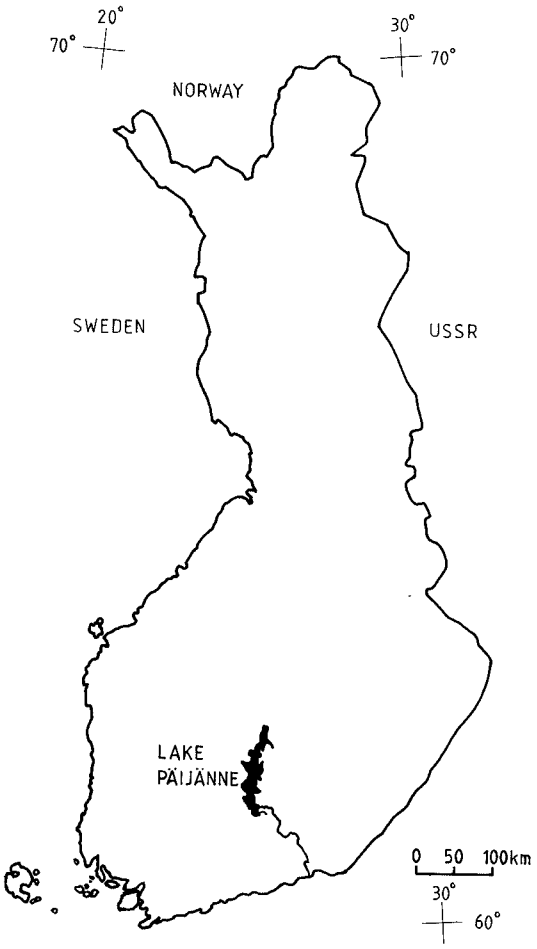



Fig. 11. Lake Päijänne is situated in central Finland.

with the river Jämsänjoki (Fig. 12). The effluents of the town of Jyväskylä also load the northernmost part of the lake (the Nenäniemi treatment plant). Changes carried out in the factories of Äänekoski decreased the BOD loading remarkably in the early 1980s. Lake Päijänne has several smaller loading sources (see e.g. Frisk 1979). However, the effects of smaller point loadings as well as the diffuse loading and natural leaching are not great. One problem in describing Lake Päijänne with the models is caused by the bay consisting of the areas of Lehtiselkä and Tiirinselkä. These areas were not treated in this study, but the models were tested against data of the so-called Trunk-Päijänne only. In the same way as in the application of Lake Haukivesi the bays that do not participate in the change of water in the stream were excluded. The same methodology has been applied in the mass balance studies of Lake Päijänne carried out by the Hydrobiological Research Institute, nowadays the

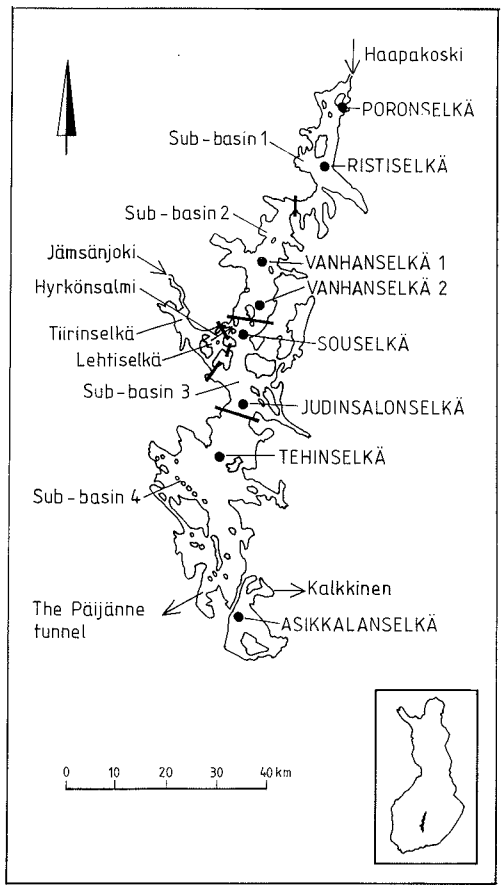



Fig. 12. The sub-basins and the sampling points of Lake Päijänne used in this study.

Institute for Environmental Research at the University of Jyväskylä (e.g. Lappalainen and Mäkinen 1974, Granberg and Mäkinen 1976, Mäkinen and Granberg 1977) and also in the studies of Frisk (1978, 1979) and Frisk et al. (1981).

Lake Päijänne is undoubtedly one of the most thoroughly investigated lakes in Finland, thanks greatly to the Institute for Environmental Research at the University of Jyväskylä. Phosphorus models for Lake Päijänne have been applied by Lappalainen (1972), Granberg (1977), Frisk (1978, 1979) and Lappalainen et al. (1979). The sub-basins and the sampling points used in this study are presented in Fig. 12.

The methods of data processing in calculating the input data needed in the models were mainly similar to those used in the case of Lake Haukivesi. The data of the years 1970—1973 and 1975—1986 was used. There were difficulties in formulating mass balances for the year 1974, due to unusual discharge conditions, and therefore mass balances were not calculated for that year by the Hydrobiological Research Center (Granberg, pers. comm.). For the same reason the year 1974 was also excluded from this study. However, a time series of 16 years must be considered exceptionally long in mass balance studies.

The input discharge values were obtained from the Hydrological Office of the National Board of Waters and the Environment. The input discharges from the nearest drainage areas were estimated on the basis of the surface areas and average runnoff values (Appendix 2).

The system layout of Lake Päijänne is presented in Fig 13. The effective volumes of the sub-basins (Table 3) have been estimated in the study of Lappalainen and Mäkinen (1974).

The concentration values were obtained from the Water and Environment District of Central Finland and from the water quality data bank of the National Board of Waters and the Environment. Both time and volume weighting were used in calculating the average concentrations (Appendix 2).

The phosphorus inputs coming from the nearest drainage areas were calculated taking advantage of the study of Kauppi (1978). Input with the precipitation was taken from the studies of Lappalainen and Mäkinen (1974), Järvinen and Haapala (1980) and Järvinen (1986). The $\Delta I_i$ values represent the sum of the diffuse loading factors including natural leaching, input with precipitation and small point loads and small rivers (Appendix 2).

The loading values of the factories and the municipalities were taken from the study of Frisk (1979) and obtained from the Water and Environ-

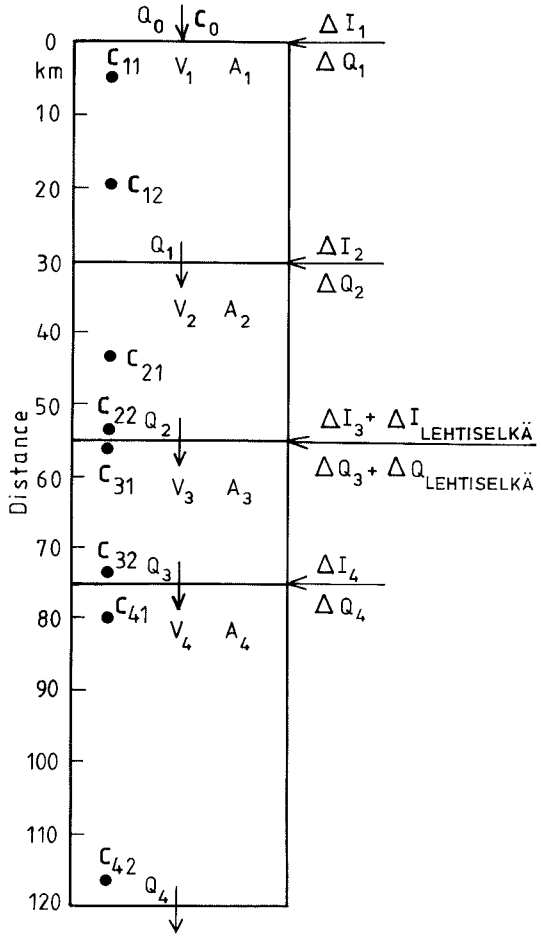



Fig. 13. The system layout of Lake Päijänne. $c_0$ = mixing concentration of phosphorus at the beginning of sub-basin 1, calculated using the data of Haapakoski, Äijälänsalmi and the treatment plant of Nenäniemi (town of Jyväskylä with suburbs), $Q_0$ = inflow, $\Delta Q_i$ = additional flow, $\Delta I_i$ = additional input, $V_i$ = volume, $c_{i1}$ and $c_{i2}$ = concentrations. The values of $V_i$ have been presented in Table 3 and the values of $c_0$, $Q_0$, $c_{i1}$, $c_{i2}$, $\Delta Q_i$ and $\Delta I_i$ in Appendix 2.

ment District of Central Finland. The phosphorus inputs of the rivers were partly taken from the reports made by the Environmental Research Institute of the University of Jyväskylä (Granberg et al. 1978, 1979, 1981, 1982, 1986, Granberg 1980, Granberg and Mäkelä 1986) and Suunnittelukeskus Oy (1983, 1984) and parlty calculated on the basis of discharge and concentration values obtained from the Hydrological Office and the Water and Environment District of Central Finland. The additional input coming from the area of Lehtiselkä (Fig. 12) is very difficult to assess exactly, because water flows back and forth between Lehtiselkä and Trunk-Päijänne. Lappalainen and Mäkinen (1974) suggested a method to describe this phenomenon. According to these authors about 26 % of the discharge of Trunk-Päijänne flows to Lehtiselkä via Hyrkönsalmi. This flow must be added to the "ordinary" flow of Lehtiselkä and the total output of phosphorus is then calculated as the product of this total discharge and the observed concentrations of the sampling point of Lehtiselkä. This method has been used by the Environmental Research Institute and by Frisk (1979) and was also applied in this study. The additional input from Lehtiselkä was calculated as the difference between the total output from Lehtiselkä to Trunk-Päijänne and the input from Trunk-Päijänne to Lehtiselkä, assessed using the observed concentrations of Souselkä (Fig. 12). There is considerable uncertainty in the input values from Lehtiselkä, because the method tends to oversimplify the situation.

Table 3. The morphometric data of the sub-basins of Lake Päijänne (Fig. 13). The locations of the sampling points are expressed in kilometres downstream from the beginning of the sub-basin. The sampling point of Vanhanselkä 1 is the same as point 610 and the sampling point of Vanhanselkä 2 point 625. The sampling point of Souselkä is point 638 until 1977 and point 640 since 1978, the numbers referring to those used by the Hydrobiological Research Institute of Jyväskylä.

| Sub-basin number | Effective volume $10^6$ m$^3$ | Effective area km$^2$ | Length km | Sampling point | Location of the sampling point, km |
|---|---|---|---|---|---|
| 1 | 2150 | 142 | 30 | Poronselkä | 5 |
| | | | | Ristiselkä | 20 |
| 2 | 2800 | 166 | 25 | Vanhanselkä 1 | 13 |
| | | | | Vanhanselkä 2 | 23 |
| 3 | 2000 | 143 | 20 | Souselkä | 2 |
| | | | | Judinsalonselkä | 18 |
| 4 | 7200 | 582 | 45 | Tehinselkä | 10 |
| | | | | Asikkalanselkä | 43 |

## 4.2 Testing of the models

### 4.2.1 Lake Haukivesi

As presented in Section 4.12, Lake Haukivesi was divided into six sub-basins. The models were tested using two divisions:

— as six sub-basins according to Figs. 9 and 10
— as two sub-basins that were formed by combining sub-basins 1 and 2 into sub-basin 1 and the others into sub-basin 2.

It was not considered to be realistic to apply the models without any sub-basin division, because the major discharge of Tappuvirta (see Fig. 9) has such a great effect on phosphorus concentrations. The models were calibrated using the same sedimentation coefficients for the whole lake. The coefficients for the different sub-basins were not calculated.

For calculating the concentrations in the different sub-basins the discharge values of the sub-basins are needed. These were calculated by means of an elementary water balance equation:

$$Q_i = Q_{i-1} + \Delta Q_i \tag{86}$$

where

$Q_i$ = outflow discharge of sub-basin i ($Q_0$ = discharge coming from the sub-basin not considered in this study (Figs. 9 and 10)
$\Delta Q_i$ = additional discharge to sub-basin i, consisting of the effects of the nearest drainage area and the difference between precipitation and evaporation

The modifications presented in Section 3 can be classified as single (C1, PN1, PA1, C2, PN2, PA2) and combined (PCN1, PCA1, PCN2, PCA2). As described in Section 3 the combined modifications are linear combinations of single modifications.

In applying the models an important distinction must be made between modifications with and without additional input. In calculating the initial concentration for the modifications C1, PN1, C2 and PN2 the following formula was used:

$$Q_{0i} = \frac{Q_{i-1}\, c_{i-1} + \Delta I_i}{Q_i} \tag{87}$$

where

$c_{0i}$ = for plug flow modifications (PN1, PN2) the concentration at the beginning of the sub-basin and for CSTR modifications (C1 and C2) the mixing concentration (= input to the sub-basin divided by the discharge of the sub-basin)
$\Delta I_i$ = additional input to sub-basin i

For the modifications with additional input (PA1, PA2)

$$c_{0i} = c_{bi-1} \tag{88}$$

where

$c_{bi-1}$ = concentration at the outlet of sub-basin i−1

In the application with only two sub-basins the additional input from Tappuvirta was located to the beginning of sub-basin 2 according to Eq. (87) even when modifications with additional input were considered, because sub-basin 2 is very long in this division.

In the test the data set of the years 1976—1985 was used. The models were calibrated, i.e. the sedimentation coefficients (k and a) were calculated for the different modifications. Both voluminal and areal versions (see Section 3.1) were applied. Three types of calibrations were carried out, using

— the average data of the whole period
— annual data
— the whole data

### 4.2.2 Lake Päijänne

Two sub-basin divisions were also used in the application to Lake Päijänne:

— as four sub-basins (Figs. 12 and 13)
— as two sub-basins that were formed by combining sub-basins 1 and 2 into sub-basin 1 and the others into sub-basin 2

As in the case of Lake Haukivesi, the application to the whole lake was not considered realistic, because the area of Lehtiselkä (see Fig. 12) has a considerable effect on water quality in central and southern parts of Lake Päijänne. The additional input from Lehtiselkä was located at the beginning of the sub-basin.

For calculating the discharge values of the different sub-basins a more accurate method than in the case of Lake Haukivesi could be used, because the discharge values of the outlets of Lake Päijänne (Kalkkinen and the Päijänne tunnel) are continuously measured. Equation (86) was applied but $\Delta Q_i$ values were calculated using the method already used by Lappalainen and Mäkinen (1974):

$$\Delta Q_i = A_{ri}\, q_{ri} + \frac{A_i}{\Sigma A_i}(Q_K + Q_P - (\Sigma Q_{Ji} + \Sigma A_{ri}\, q_{ri})) \tag{89}$$

where

$\Delta Q_i$ = additional input to sub-basin i, including the effect of the nearest drainage area ($A_{ri}$

= area, $q_{ri}$ = runoff) and the effect of precipitation, evaporation and the so-called lag-time flow and the errors in determination of discharge values
$Q_K$ = discharge of Kalkkinen
$Q_P$ = discharge of the Päijänne tunnel
$A_i$ = area of sub-basin i
$\Sigma Q_{Ji}$ = sum of the input discharges of the rivers

Otherwise the methods of the application were similar to those used in the application to Lake Haukivesi. The data sets of the years 1970—1973 and 1975—1986 was used. The calibrations were carried out using:
— the average data of the wole period 1970—1986 (excluding 1974)
— data of the four-year periods 1970—1973, 1975—1978, 1979—1982 and 1983—1986
— the whole data

Data of four-year periods were used instead of annual data, because the theoretical detention time of Lake Päijänne is long, about 2.7 years (for Lake Haukivesi only about 0.5 years).

### 4.2.3 Measuring the applicability of the models

In the calibration of the models a function based on the sum of the squares of the differences between the calculated and observed values was used:

$$f = \Sigma(c_{calc} - c_{obs})^2 \quad (90)$$

where
$c_{calc}$ = concentration calculated by means of the model
$c_{obs}$ = observed concentration

In the comparison between data sets with different numbers of observations the comparison can be using the ratio f/n, where n is the number of observations. The sedimentation coefficients were assumed to be the same for all sub-basins and thus the explicit formulae presented in Section 3 could not be used in the calculation of their values but an iterative method had to be used.

Another way of measuring the applicability of the models is to calculate the mean absolute difference that gives information on the average error in model predictions:

$$d_{ma} = \frac{\Sigma|c_{calc} - c_{obs}|}{n} \quad (91)$$

where
$d_{ma}$ = mean absolute difference between calculated and observed values
n = number of observations

In order to assess the effect of the sedimentation term the following ratios were calculated:

$$q_f = \frac{f_i}{f_c} \quad (92)$$

and

$$q_d = \frac{d_i}{d_c} \quad (93)$$

where
$f_i$ = value of f (Eq. 90) calculated using model modification i
$f_c$ = value of f calculated using the corresponding conservative modification
$d_i$ = value of $d_{ma}$ (Eq. 91) calculated using model modification i
$d_c$ = value of $d_{ma}$ calculated using the corresponding conservative model modification

The rations $q_f$ and $q_d$ give information on how successful the description of the phosphorus retention process has been, while in the values of f and $d_{ma}$ the effect of the error due to hydraulic description is also included.

# 5 RESULTS

## 5.1 General

The results of the application of the models to Lake Haukivesi are presented in Section 5.2 and to Lake Päijänne in Section 5.3. The symbols and units used in the results in Tables 4—28 are the following:
k = first order voluminal sedimentation coefficient, $a^{-1}$
$k_a$ = first order areal sedimentation coefficient, m $a^{-1}$
a = second order voluminal sedimentation coefficient, $mg^{-1}$ $m^3$ $a^{-1}$
$a_a$ = second order areal sedimentation coefficient, $mg^{-1}$ $m^4$ $a^{-1}$
f = sum of the squares of the differences between the calculated and observed concentrations (Eq. 90), $mg^2$ $m^{-6}$
n = number of observations
$d_{ma}$ = mean absolute difference between the

calculated and observed concentrations (Eq. 91), mg $m^{-3}$

$q_f$ = ratio of the value f calculated using the model to that calculated using the corresponding conservative model (Eq. 92)

$q_d$ = ratio of the value $d_{ma}$ calculated using the model to that calculated using the corresponding conservative model (Eq. 93)

D = plug flow coefficient in combined model modifications, the value 1 indicating plug flow (PFR) and the value 0 total mixing (CSTR)

The different model modifications (C1, C2, PN1, PN2, PA1, PA2, PCN1, PCN2, PCA1 and PCA2) were presented in Section 3 (see Table 1). In addition, there are two conservative modifications, one corresponding to models with no additional input (CONS1) and the other corresponding to models with additional input (CONS2). The conservative models are used in evaluating the successfulness of the description of sedimentation.

Table 4. The results of the application of the two conservative modifications to Lake Haukivesi (as six sub-basins) using the annual data for 1976—1985. The values in the table are average values, annual values are given in Appendix 3.

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 17.72 | 1 | 3.58 | 1 |
| CONS2 | 0 | 20.69 | 1 | 4.06 | 1 |

Table 5. The results of the application of the different modifications to Lake Haukivesi (as six-sub-basins) using the annual data for 1976—1985. The values in the table are average values, annual values are given in Appendix 3.

a) voluminal versions

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 1.79 | 1.19 | 0.07 | 0.92 | 0.25 |
| PN1 | 2.09 | 1.73 | 0.10 | 1.01 | 0.28 |
| PA1 | 2.17 | 1.84 | 0.09 | 1.01 | 0.25 |
| C2 | 0.116 | 2.08 | 0.12 | 1.17 | 0.33 |
| PN2 | 0.155 | 1.21 | 0.07 | 0.96 | 0.27 |
| PA2 | 0.156 | 0.90 | 0.04 | 0.81 | 0.20 |

b) areal versions

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 19.0 | 1.60 | 0.09 | 1.02 | 0.28 |
| PN1 | 22.8 | 1.33 | 0.08 | 0.98 | 0.27 |
| PA1 | 23.6 | 1.11 | 0.05 | 0.88 | 0.22 |
| C2 | 1.14 | 2.88 | 0.17 | 1.40 | 0.39 |
| PN2 | 1.42 | 1.77 | 0.10 | 1.07 | 0.28 |
| PA2 | 1.44 | 1.26 | 0.06 | 0.88 | 0.22 |

## 5.2 Lake Haukivesi

### 5.2.1 Lake Haukivesi as six sub-basins

In the application of the models to the annual data of the whole period (1976—1985) the following results were obtained (Tables 4 and 5).

The results of the application of the models using the whole data of the years 1976—1985 simultaneously are presented in Table 6. In conservative modifications k is always = 0 and so the conservative results are the same as in Table 4.

The results of the application of the models using the average data of the whole period (1976—1985) are presented in Tables 8 and 9.

The principal differences between the different modifications are the following. When CSTR modifications (C1 or C2) are used the concentration remains the same along the whole sub-basin, whereas in the PFR modifications the concentration decreases in each sub-basin. The difference between modifications without additional input (PN1 and PN2) and with additional input (PA1 and PA2) is that in the latter modifications the curve describing concentration is continuous. A continuous curve must be considered realistic in lakes like Haukivesi where the boundaries of the sub-basins are not very clear. In Figs. 14 and 15 only the results of the voluminal versions are presented because the corresponding figures for the areal versions would be practically identical.

The combination of PFR and CSTR does not add very much to the suitability of the models (Table 10, Fig. 16). However, there is a difference

Table 6. The results of the application of the different model modifications to Lake Haukivesi (as six sub-basins) using the whole data (1976—1985).

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 1.81 | 3.00 | 0.17 | 1.37 | 0.38 |
| PN1 | 2.11 | 3.44 | 0.19 | 1.48 | 0.42 |
| PA1 | 2.19 | 3.64 | 0.18 | 1.50 | 0.37 |
| C2 | 0.118 | 3.40 | 0.19 | 1.50 | 0.42 |
| PN2 | 0.159 | 2.44 | 0.14 | 1.26 | 0.35 |
| PA2 | 0.159 | 2.16 | 0.10 | 1.19 | 0.29 |

b) areal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 19.0 | 3.47 | 0.20 | 1.49 | 0.42 |
| PN1 | 22.9 | 3.14 | 0.18 | 1.42 | 0.40 |
| PA1 | 23.8 | 3.02 | 0.15 | 1.38 | 0.34 |
| C2 | 1.15 | 4.27 | 0.24 | 1.67 | 0.47 |
| PN2 | 1.45 | 3.09 | 0.17 | 1.43 | 0.40 |
| PA2 | 1.47 | 2.60 | 0.13 | 1.27 | 0.31 |

between first and second order models when voluminal versions are considered. In the first order models the plug flow coefficient giving the best agreement was 0.3, which indicates a great degree of mixing, whereas in the second order models it was 0.9 or 1, indicating plug flow behaviour. In areal versions plug flow was favoured (Table 10). The value of the best coefficient (k or a) is a function of D (Fig. 17).

Table 8. Application of the two conservative modifications to Lake Haukivesi (as six sub-basins) using the average data of the years 1976—1985.

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 15.26 | 1 | 3.59 | 1 |
| CONS2 | 0 | 18.15 | 1 | 4.17 | 1 |

Table 9. The results of the application of the different model modifications to Lake Haukivesi (as six sub-basins) using the average data of the years 1976—1985.

a) voluminal versions

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 1.88 | 0.49 | 0.03 | 0.65 | 0.18 |
| PN1 | 2.17 | 0.87 | 0.06 | 0.89 | 0.25 |
| PA1 | 2.25 | 1.04 | 0.06 | 0.88 | 0.21 |
| C2 | 0.123 | 1.45 | 0.10 | 1.08 | 0.30 |
| PN2 | 0.163 | 0.54 | 0.04 | 0.63 | 0.17 |
| PA2 | 0.164 | 0.29 | 0.02 | 0.46 | 0.11 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 20.0 | 0.91 | 0.06 | 0.79 | 0.22 |
| PN1 | 23.9 | 0.58 | 0.04 | 0.68 | 0.19 |
| PA1 | 24.8 | 0.44 | 0.02 | 0.55 | 0.13 |
| C2 | 1.21 | 2.24 | 0.15 | 1.35 | 0.38 |
| PN2 | 1.53 | 1.09 | 0.07 | 0.90 | 0.25 |
| PA2 | 1.55 | 0.63 | 0.03 | 0.61 | 0.15 |

Table 10. The best combined models for Lake Haukivesi as six sub-basins (average data of 1976—1985).

a) voluminal versions

| Model | D | k or a | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.3 | 1.99 | 0.429 | 0.60 |
| PCA1 | 0.3 | 2.01 | 0.324 | 0.49 |
| PCN2 | 1.0 | 0.163 | 0.544 | 0.63 |
| PCA2 | 0.9 | 0.161 | 0.274 | 0.42 |

b) areal versions

| Model | D | $k_a$ or $a_a$ | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.8 | 23.2 | 0.57 | 0.71 |
| PCA1 | 0.7 | 23.4 | 0.37 | 0.49 |
| PCN2 | 1.0 | 1.53 | 1.09 | 0.90 |
| PCA2 | 1.0 | 1.55 | 0.63 | 0.61 |

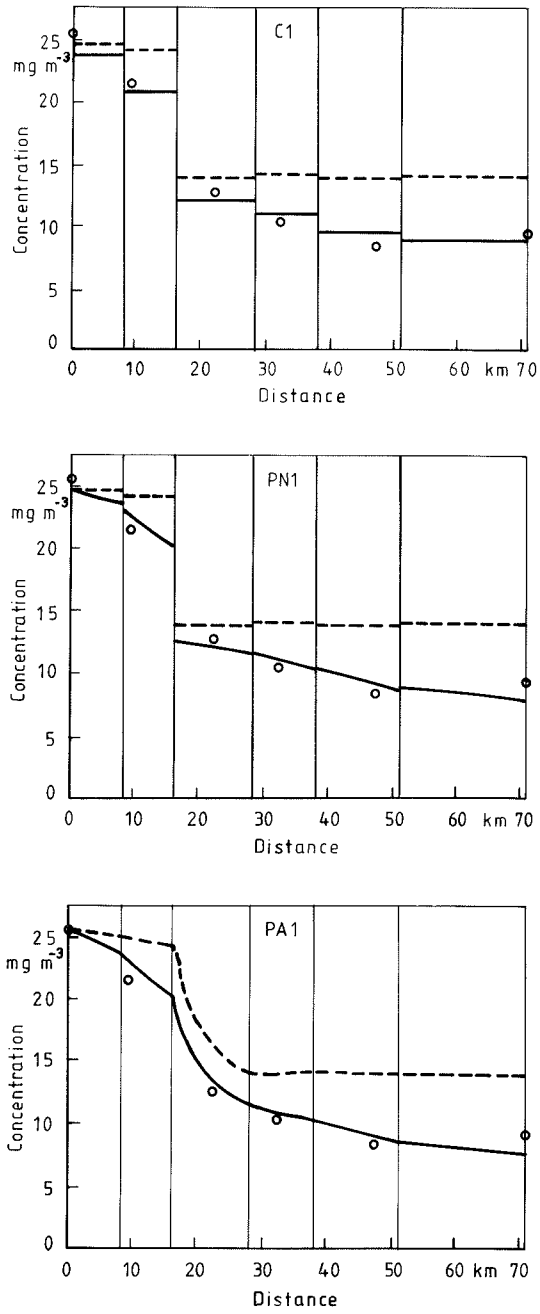
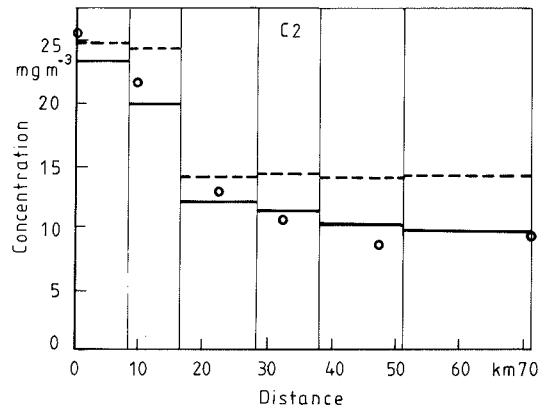
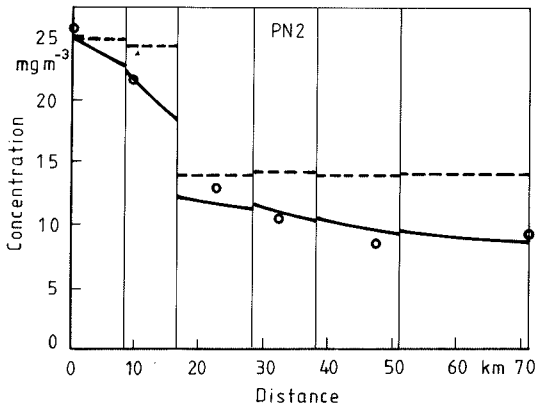



Fig. 14. Application of the first order (voluminal) modifications (C1, PN1, PA1) to Lake Haukivesi as six sub-basins (average data of 1976—1985). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.



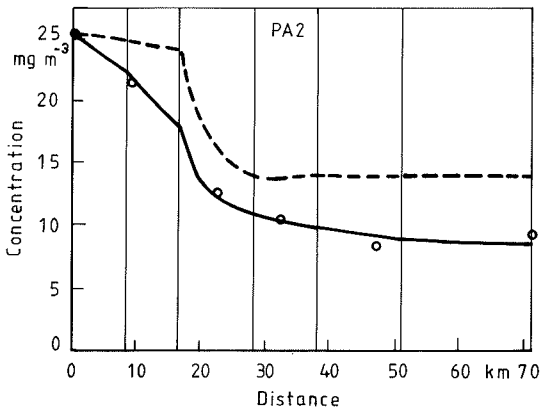




Fig. 15. Application of the second order (voluminal) modifications (C2, PN2, PA2) to Lake Haukivesi as six sub-basins (average data of 1976—1985). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.

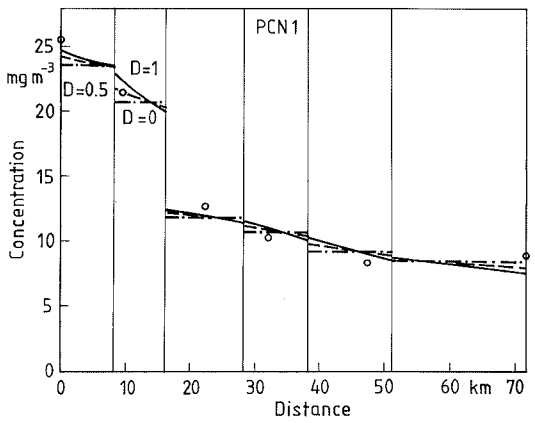



Fig. 16. Application of the combined modification PCN1 (voluminal) to Lake Haukivesi as six sub-basins (average data of 1976—1985). Curves with three values of the plug flow coefficient (D) are presented. ——— = D=1 (PFR), – – – – – = D=0.5, —·— = D=0 (CSTR), o = observed values.

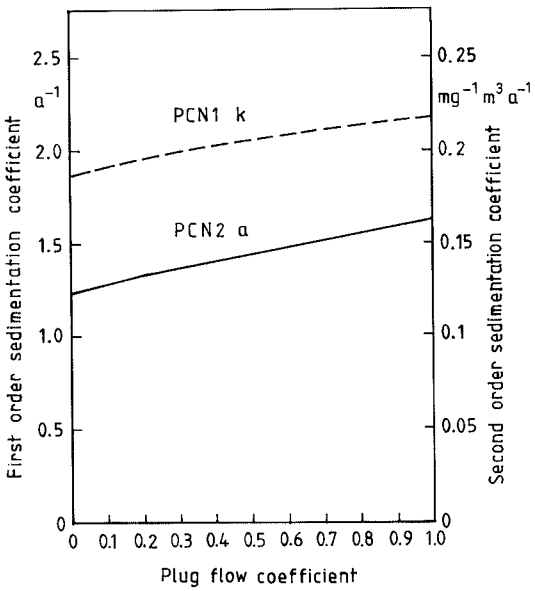



Fig. 17 The effect of the plug flow coefficient on the best sedimentation coefficient (k or a), modifications PCN1 and PCN2 (voluminal). Lake Haukivesi as six sub-basins, average data of the years 1976—1985.

### 5.2.2 Lake Haukivesi as two sub-basins

In the application of the annual data the following results were obtained (Tables 11 and 12).

The results of the application of the models to the whole data are presented in Table 13 (the results for the conservative modifications are the same as in Table 11).

The results of the application of the models to the average data of the whole period are presented in Tables 14 and 15.

In the division into six sub-basins the curves describing the concentration are continuous for modifications with additional input (Figs. 14 and 15). In the division into two sub-basins the situation is different. The additional input of water and phosphorus coming from Tappuvirta (Fig. 9) could not be considered as an additional input to sub-basin 2 because this sub-basin is very long and the input comes to the upper part of the sub-basin.

Table 11. The results of the application of the two conservative modifications to Lake Haukivesi (as two sub-basins) using the annual data of 1976—1985. The values in the table are average values, annual values are given in Appendix 3.

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 17.74 | 1 | 3.59 | 1 |
| CONS2 | 0 | 18.20 | 1 | 3.62 | 1 |

Table 12. The results of the application of the different modifications to Lake Haukivesi (as two sub-basins) using the annual data of 1976—1985. The values in the table are average values, annual values are given in Appendix 3.

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 1.30 | 2.88 | 0.16 | 1.45 | 0.40 |
| PN1 | 2.11 | 1.59 | 0.09 | 1.03 | 0.29 |
| PA1 | 2.08 | 1.65 | 0.09 | 1.06 | 0.29 |
| C2 | 0.096 | 2.98 | 0.17 | 1.48 | 0.41 |
| PN2 | 0.144 | 1.51 | 0.09 | 1.02 | 0.28 |
| PA2 | 0.138 | 1.54 | 0.08 | 1.04 | 0.29 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 14.6 | 2.86 | 0.16 | 1.45 | 0.40 |
| PN1 | 23.3 | 1.49 | 0.08 | 1.04 | 0.29 |
| PA1 | 22.8 | 1.52 | 0.08 | 1.07 | 0.30 |
| C2 | 1.01 | 3.31 | 0.19 | 1.59 | 0.44 |
| PN2 | 1.46 | 1.91 | 0.11 | 1.11 | 0.31 |
| PA2 | 1.39 | 1.92 | 0.11 | 1.13 | 0.31 |

Table 13. The results of the application of the different model modifications to Lake Haukivesi (as two sub-basins) using the whole data (1976—1985).

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 1.32 | 4.58 | 0.26 | 1.82 | 0.51 |
| PN1 | 2.12 | 3.27 | 0.18 | 1.46 | 0.41 |
| PA1 | 2.10 | 3.49 | 0.19 | 1.54 | 0.42 |
| C2 | 0.099 | 4.19 | 0.23 | 1.69 | 0.47 |
| PN2 | 0.146 | 2.74 | 0.15 | 1.30 | 0.36 |
| PA2 | 0.142 | 2.85 | 0.16 | 1.35 | 0.37 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 14.8 | 4.60 | 0.26 | 1.78 | 0.49 |
| PN1 | 22.4 | 3.23 | 0.18 | 1.43 | 0.40 |
| PA1 | 23.1 | 3.41 | 0.19 | 1.51 | 0.42 |
| C2 | 1.03 | 4.56 | 0.26 | 1.77 | 0.49 |
| PN2 | 1.48 | 3.19 | 0.18 | 1.44 | 0.40 |
| PA2 | 1.42 | 3.30 | 0.18 | 1.47 | 0.41 |

Table 14. The results of the application of the two conservative models to Lake Haukivesi (as two sub-basins) using the average data of the years 1976—1985.

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 15.39 | 1 | 3.60 | 1 |
| CONS2 | 0 | 15.57 | 1 | 3.63 | 1 |

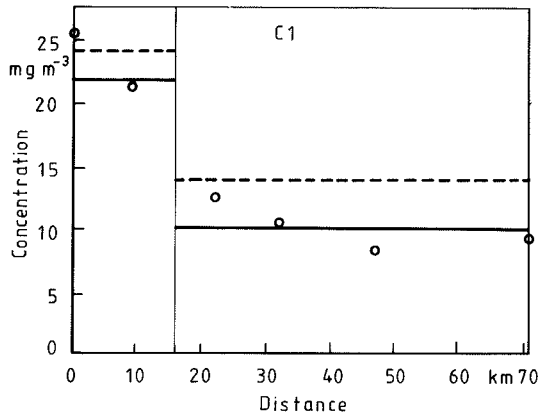
Table 15. The results of the application of the different models to Lake Haukivesi (as two sub-basins) using the average data of the years 1976—1985.

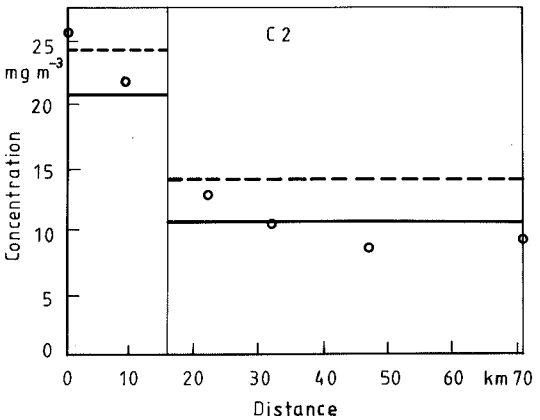
a) voluminal versions

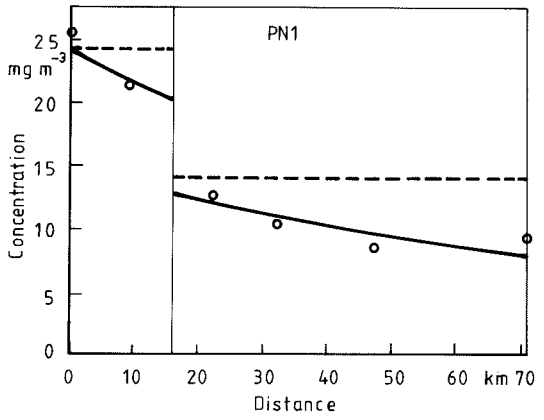
| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 1.36 | 2.24 | 0.15 | 1.21 | 0.33 |
| PN1 | 2.20 | 0.88 | 0.06 | 0.85 | 0.24 |
| PA1 | 2.17 | 0.85 | 0.05 | 0.87 | 0.24 |
| C2 | 0.102 | 2.44 | 0.16 | 1.32 | 0.37 |
| PN2 | 0.153 | 0.91 | 0.06 | 0.87 | 0.24 |
| PA2 | 0.148 | 0.86 | 0.06 | 0.79 | 0.22 |

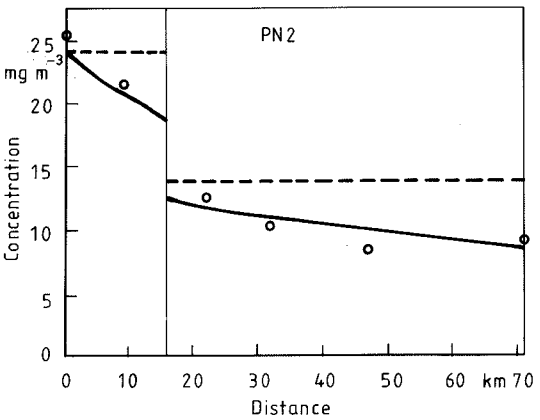
b) areal versions

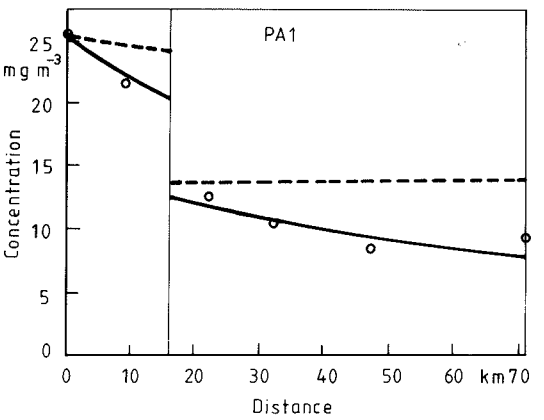
| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 15.3 | 2.25 | 0.15 | 1.21 | 0.33 |
| PN1 | 24.4 | 0.82 | 0.05 | 0.80 | 0.22 |
| PA1 | 24.0 | 0.74 | 0.05 | 0.75 | 0.21 |
| C2 | 1.07 | 2.76 | 0.18 | 1.49 | 0.41 |
| PN2 | 1.57 | 1.29 | 0.08 | 0.96 | 0.27 |
| PA2 | 1.50 | 1.22 | 0.08 | 0.94 | 0.26 |



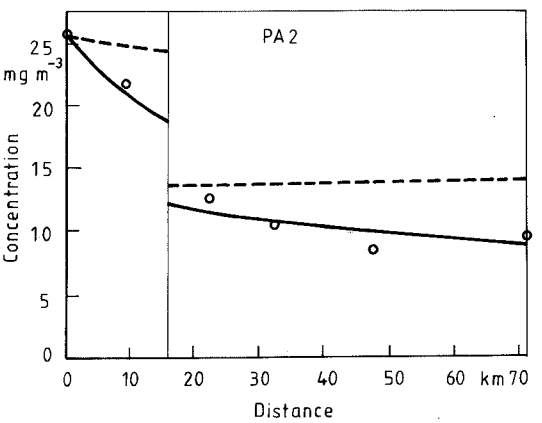




Fig. 18. Application of the first order (voluminal) modifications (C1, PN1, PA1) to Lake Haukivesi as two sub-basins (average data of 1976—1985). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.

Fig. 19. Application of the second order (voluminal) modifications (C2, PN2, PA2) to Lake Haukivesi as two sub-basins (average data of 1976—1985). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.

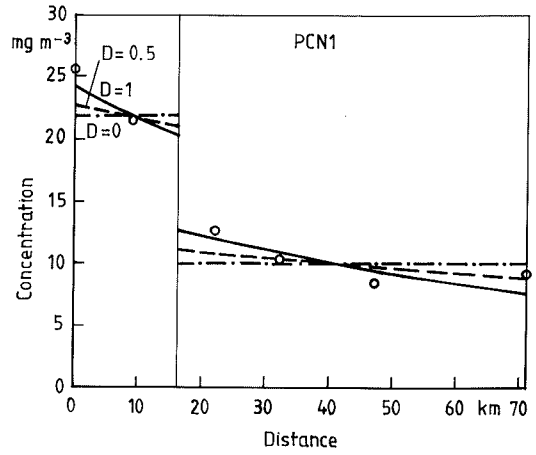



Fig. 20. Application of the combined modification PCN1 (voluminal) to Lake Haukivesi as two sub-basins (average data of 1976—1985). Curves with three values of the plug flow coefficient (D) are presented. ——— = D=1 (PFR), – – – – = D=0.5, — ·— = D=0 (CSTR), o = observed values.

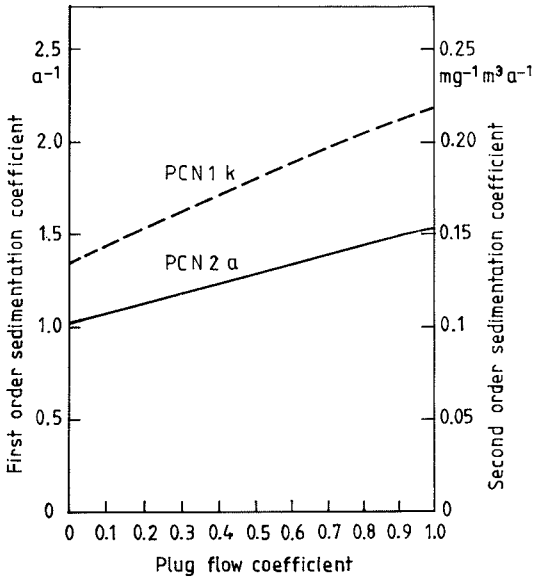



Fig. 21 The effect of the plug flow coefficient on the best sedimentation coefficient (k or a), modifications PCN1 and PCN2 (voluminal). Lake Haukivesi as two sub-basins, average data of 1976—1985.

Table 16. The best combined models for Lake Haukivesi as two sub-basins (average data of 1976—1985).

a) voluminal versions

| Model | D | k or a | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.8 | 2.05 | 0.81 | 0.79 |
| PCA1 | 0.9 | 2.10 | 0.83 | 0.84 |
| PCN2 | 1.0 | 0.153 | 0.91 | 0.87 |
| PCA2 | 1.0 | 0.148 | 0.87 | 0.79 |

b) areal versions

| Model | D | $k_a$ or $a_a$ | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.9 | 23.6 | 0.80 | 0.79 |
| PCA1 | 1.0 | 24.0 | 0.74 | 0.75 |
| PCN2 | 1.0 | 1.57 | 1.27 | 0.96 |
| PCA2 | 1.0 | 1.50 | 1.22 | 0.94 |

The input from Tappuvirta was therefore also treated as part of the initial input when the modifications with additional input were considered. This has a significant effect on the shapes of the concentration curves (Figs. 18 and 19).

The division into two sub-basins means in practice that there is considerable areal variation of water quality inside the sub-basins. Therefore it is quite clear that PFR models tend to give better agreement with observed data than CSTR models. In the application of the combined models (PCN1, PCN2, PCA1, PCA2) the best plug flow coefficients were rather large, 0.8—1, indicating the plug flow behaviour (Table 16). The effect of the plug flow coefficient on concentration can be seen in Fig. 20. The effect of the plug flow coefficient on the best sedimentation coefficient (k or a) is greater than in the case of division into six sub-basins (Fig. 21).

## 5.3 Lake Päijänne

### 5.3.1 Lake Päijänne as four sub-basins

Because the theoretical detention time of Lake Päijänne is long (about 2.7 years), annual data was not used, but the models were applied using data of four-year periods (Tables 17 and 18).

The application of the models using the whole data of the years 1970—1973 and 1975—1986 gave the following results (Table 19). The conservative results are the same as in Table 17.

The results of the application of the models to the average data of all years are presented in Tables 20 and 21.

The observed concentrations and the concentrations calculated using the voluminal modifications are presented in Figs. 22 and 23. The areal modifications would produce practically identical results.

In the northern sub-basin of Lake Päijänne the concentration is always much greater at sampling point 1 than at point 2 (Figs. 22, 23 and 24) and therefore the CSTR description does not give realistic results. PFR modifications gave smaller f/n

Table 17. The results of the application of the two conservative modifications to Lake Päijänne (as four sub-basins) using data of the four-year periods 1970—1973, 1975—1978, 1979—1982 and 1983—1986. The values in the table are average values, values for the different periods are given in Appendix 4.

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 206.9 | 1 | 13.1 | 1 |
| CONS2 | 0 | 207.3 | 1 | 13.0 | 1 |

Table 18. The results of the application of the different modifications to Lake Päijänne (as four sub-basins) using data of the four-year periods 1970—1973, 1975—1978, 1979—1982 and 1983—1986. The values in the table are average values, values for the different periods are given in Appendix 4.

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 0.76 | 5.19 | 0.03 | 1.55 | 0.12 |
| PN1 | 0.85 | 3.24 | 0.02 | 1.51 | 0.12 |
| PA1 | 0.84 | 2.29 | 0.01 | 1.23 | 0.09 |
| C2 | 0.047 | 6.48 | 0.03 | 1.53 | 0.12 |
| PN2 | 0.050 | 1.65 | 0.01 | 1.01 | 0.08 |
| PA2 | 0.049 | 1.05 | 0.01 | 0.76 | 0.06 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 11.4 | 5.91 | 0.03 | 1.85 | 0.14 |
| PN1 | 13.0 | 4.23 | 0.02 | 1.63 | 0.12 |
| PA1 | 12.8 | 3.20 | 0.02 | 1.43 | 0.11 |
| C2 | 0.70 | 6.35 | 0.03 | 1.56 | 0.12 |
| PN2 | 0.76 | 1.64 | 0.01 | 1.05 | 0.08 |
| PA2 | 0.75 | 1.02 | 0.00 | 0.79 | 0.06 |

Table 19. The results of the application of the different model modifications to Lake Päijänne (as four sub-basins) using the whole data (1970—1973 and 1975—1986).

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 0.76 | 5.26 | 0.03 | 1.59 | 0.12 |
| PN1 | 0.86 | 3.35 | 0.02 | 1.51 | 0.12 |
| PA1 | 0.84 | 2.40 | 0.01 | 1.27 | 0.10 |
| C2 | 0.045 | 6.61 | 0.03 | 1.56 | 0.12 |
| PN2 | 0.049 | 1.91 | 0.01 | 1.14 | 0.09 |
| PA2 | 0.048 | 1.28 | 0.01 | 0.91 | 0.07 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 11.4 | 5.98 | 0.03 | 1.88 | 0.14 |
| PN1 | 13.0 | 4.34 | 0.02 | 1.64 | 0.13 |
| PA1 | 12.8 | 3.31 | 0.02 | 1.47 | 0.11 |
| C2 | 0.68 | 6.55 | 0.03 | 1.58 | 0.12 |
| PN2 | 0.74 | 1.90 | 0.01 | 1.17 | 0.09 |
| PA2 | 0.73 | 1.25 | 0.01 | 0.93 | 0.07 |

Table 20. Application of the two conservative modifications to Lake Päijänne (as four sub-basins) using the average data of all years (1970—1973 and 1975—1986).

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 197.6 | 1 | 12.9 | 1 |
| CONS2 | 0 | 198.0 | 1 | 12.9 | 1 |

Table 21. The results of the application of the different model modifications to Lake Päijänne (as four sub-basins) using the average data of all years (1970—1973 and 1975—1986).

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 0.77 | 4.65 | 0.02 | 1.50 | 0.12 |
| PN1 | 0.86 | 2.81 | 0.01 | 1.39 | 0.11 |
| PA1 | 0.84 | 1.88 | 0.01 | 1.08 | 0.08 |
| C2 | 0.047 | 5.84 | 0.03 | 1.49 | 0.12 |
| PN2 | 0.050 | 1.31 | 0.01 | 0.93 | 0.07 |
| PA2 | 0.049 | 0.70 | 0.00 | 0.65 | 0.05 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 11.5 | 5.35 | 0.03 | 1.82 | 0.14 |
| PN1 | 13.1 | 3.77 | 0.02 | 1.48 | 0.11 |
| PA1 | 12.9 | 2.75 | 0.01 | 1.22 | 0.09 |
| C2 | 0.70 | 5.78 | 0.03 | 1.46 | 0.11 |
| PN2 | 0.76 | 1.29 | 0.01 | 1.00 | 0.08 |
| PA2 | 0.75 | 0.67 | 0.00 | 0.71 | 0.05 |

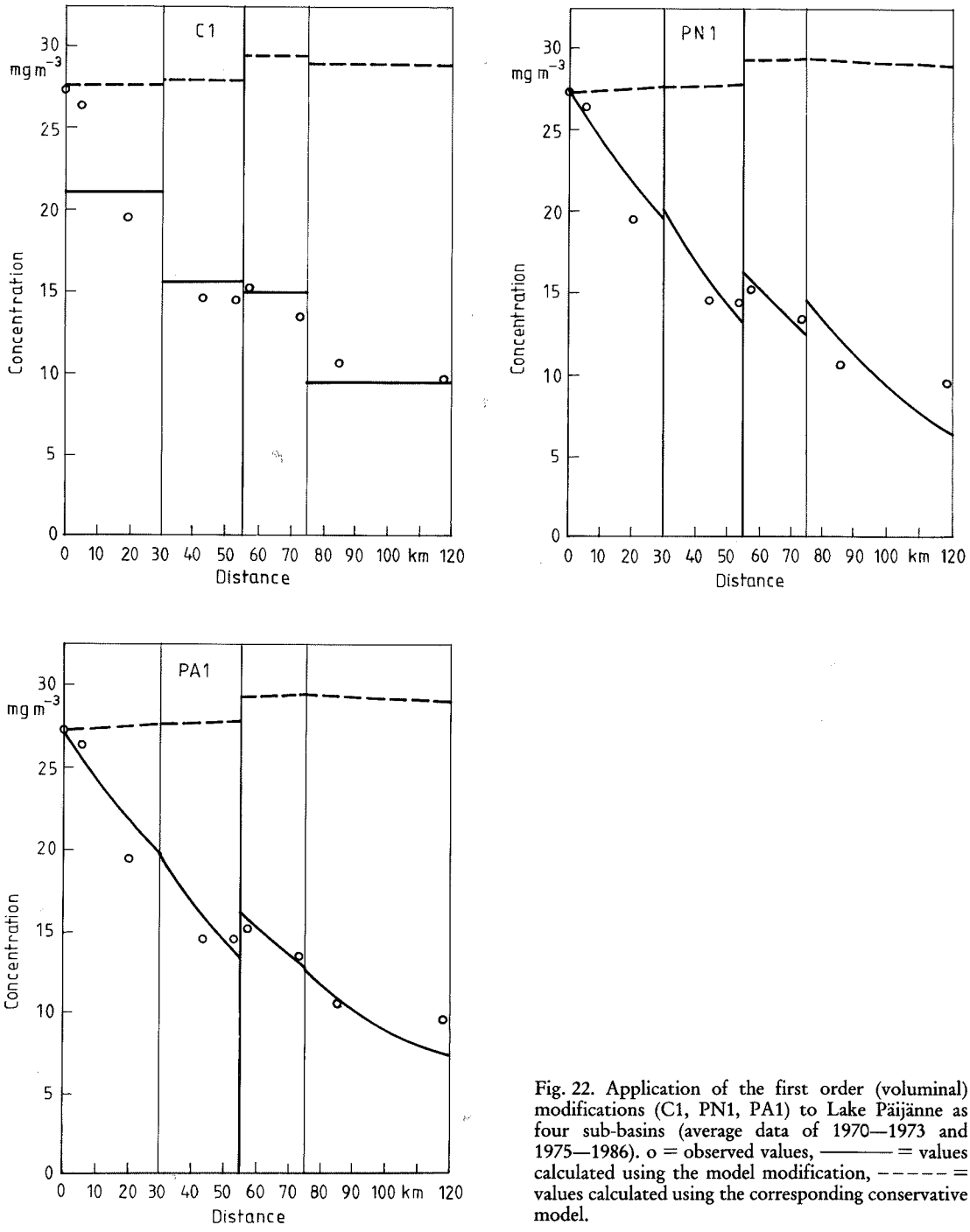



Fig. 22. Application of the first order (voluminal) modifications (C1, PN1, PA1) to Lake Päijänne as four sub-basins (average data of 1970—1973 and 1975—1986). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.

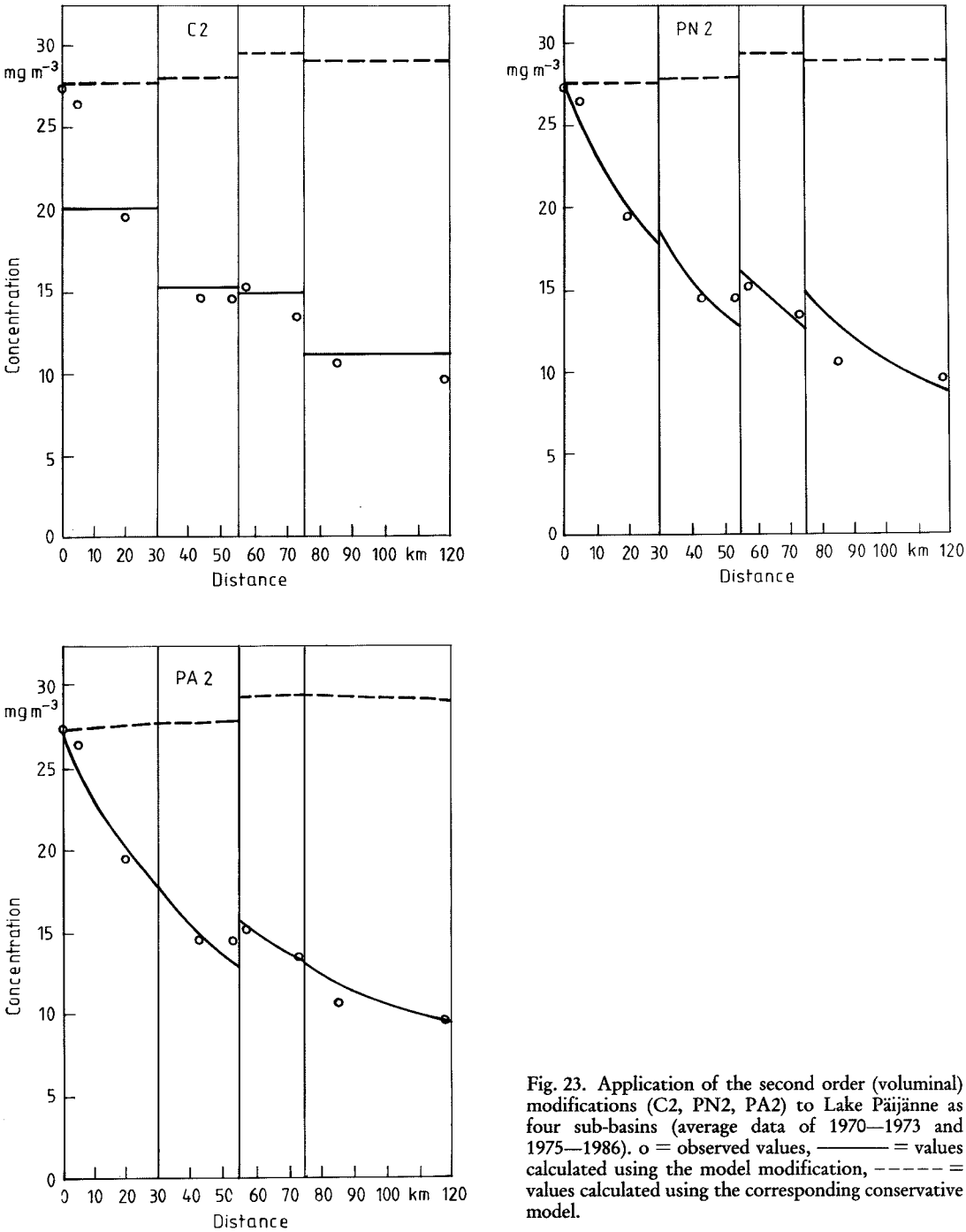



Fig. 23. Application of the second order (voluminal) modifications (C2, PN2, PA2) to Lake Päijänne as four sub-basins (average data of 1970—1973 and 1975—1986). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.

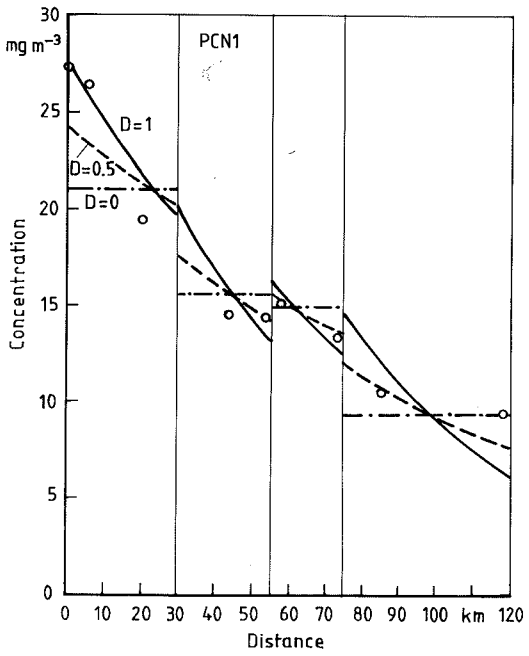



Fig. 24. Application of the combined modification PCN1 (voluminal) to Lake Päijänne as four sub-basins (average data of 1970—1973 and 1975—1986). Curves with three values of the plug flow coefficient (D) are presented. ——— = D=1 (PFR), – – – – = D=0.5, — · — · = D=0 (CSTR), o = observed values.

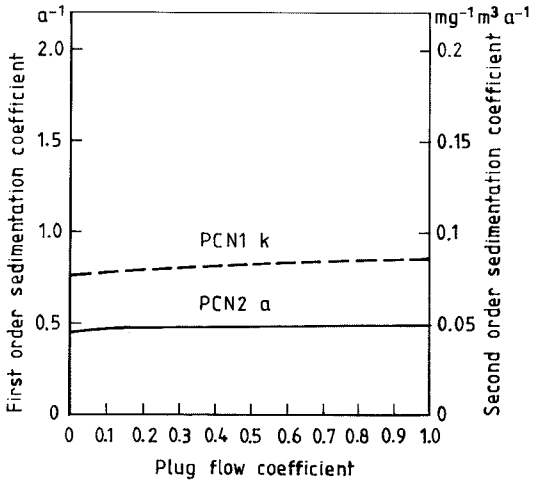



Fig. 25. The effect of the plug flow coefficient on the best sedimentation coefficient (k or a), modifications PCN1 and PCN2 (voluminal). Lake Päijänne as four sub-basins, average data of 1970—1973 and 1975—1986.

Table 22. The best combined models for Lake Päijänne as four sub-basins (average data of 1970—1973 and 1975—1986).

a) voluminal versions

| Model | D | k or a | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.7 | 0.84 | 2.09 | 1.17 |
| PCA1 | 0.8 | 0.84 | 1.73 | 1.10 |
| PCN2 | 0.9 | 0.050 | 1.29 | 0.91 |
| PCA2 | 1.0 | 0.049 | 0.70 | 0.65 |

b) areal versions

| Model | D | k or a | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.6 | 12.6 | 2.85 | 1.31 |
| PCA1 | 0.8 | 12.7 | 2.53 | 1.25 |
| PCN2 | 0.9 | 0.76 | 1.25 | 0.97 |
| PCA2 | 1.0 | 0.75 | 0.67 | 0.71 |

values and in the best modifications the plug flow coefficient D was 0.6—1.0 (Table 22). However, D had a very weak effect on the values of sedimentation coefficients a and k (Fig. 25).

### 5.3.2 Lake Päijänne as two sub-basins

In the application using the data of four-year periods the following results were obtained (Tables 23 and 24).

The application of the models using the whole data of the years 1970—1973 and 1975—1986 gave the following results (Table 25). The conservative results are the same as in Table 23.

The results of the application of the models using the average data of all years are presented in Tables 26 and 27.

The observed concentrations and the concentrations calculated using the voluminal modifications are presented in Figs. 26 and 27. The areal modifications would produce similar results.

When Lake Päijänne was considered as two sub-basins the areal variation within the sub-basins was so great that CSTR models did not give realistic descriptions (Figs. 26, 27 and 28). The best plug flow coefficient D was 0.8—1.0 (Table 28). The effect of D on the values of the sedimentation coefficients a and k was slightly stronger than in the case of four sub-basins (Fig. 29).

Table 23. The results of application of the two conservative modifications to Lake Päijänne (as two subbaisns) using data of the four-year periods 1970—1973, 1975—1978, 1979—1982 and 1983—1986. The values in the table are average values, values for the different periods are given in Appendix 4.

| Model | k | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 204.4 | 1 | 13.0 | 1 |
| CONS2 | 0 | 205.8 | 1 | 13.0 | 1 |

Table 24. The results of the application of the different modifications to Lake Päijänne (as two sub-basins) using data of the four-year periods 1970—1973, 1975—1978, 1979—1982 and 1983—1986. The values in the table are average values, values for the different periods are given in Appendix 4.

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 0.59 | 15.01 | 0.07 | 3.09 | 0.24 |
| PN1 | 0.84 | 3.25 | 0.02 | 1.45 | 0.11 |
| PA1 | 0.80 | 1.67 | 0.01 | 1.12 | 0.09 |
| C2 | 0.037 | 16.23 | 0.08 | 3.13 | 0.24 |
| PN2 | 0.047 | 1.79 | 0.01 | 1.01 | 0.08 |
| PA2 | 0.046 | 1.11 | 0.01 | 0.73 | 0.06 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 8.5 | 14.82 | 0.07 | 3.07 | 0.23 |
| PN1 | 12.6 | 4.52 | 0.02 | 1.70 | 0.13 |
| PA1 | 12.0 | 2.85 | 0.01 | 1.41 | 0.11 |
| C2 | 0.55 | 13.71 | 0.07 | 3.10 | 0.24 |
| PN2 | 0.73 | 1.81 | 0.01 | 1.04 | 0.08 |
| PA2 | 0.75 | 1.02 | 0.00 | 0.76 | 0.06 |

Table 25. The results of the application of the different model modifications to Lake Päijänne (as two sub-basins) using the whole data (1970—1973 and 1975—1986).

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 0.59 | 15.06 | 0.07 | 3.09 | 0.23 |
| PN1 | 0.84 | 3.25 | 0.02 | 1.44 | 0.11 |
| PA1 | 0.80 | 1.77 | 0.01 | 1.12 | 0.09 |
| C2 | 0.036 | 16.23 | 0.08 | 3.20 | 0.25 |
| PN2 | 0.047 | 2.14 | 0.01 | 1.24 | 0.09 |
| PA2 | 0.049 | 1.38 | 0.01 | 0.90 | 0.07 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 8.6 | 14.87 | 0.07 | 3.07 | 0.24 |
| PN1 | 12.6 | 4.62 | 0.02 | 1.75 | 0.13 |
| PA1 | 12.0 | 2.95 | 0.01 | 1.46 | 0.11 |
| C2 | 0.53 | 15.47 | 0.08 | 3.15 | 0.24 |
| PN2 | 0.71 | 2.13 | 0.01 | 1.26 | 0.10 |
| PA2 | 0.68 | 1.28 | 0.01 | 0.87 | 0.07 |

Table 26. Application of the two conservative modifications to Lake Päijänne (as two sub-basins) using the average data of all years (1970—1973 and 1975—1986).

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| CONS1 | 0 | 195.2 | 1 | 12.9 | 1 |
| CONS2 | 0 | 196.7 | 1 | 12.9 | 1 |

Table 27. The results of the application of the different model modifications to Lake Päijänne (as two sub-basins) using the average data of all years (1970—1973 and 1975—1986).

a) voluminal versions

| Model | k or a | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 0.59 | 14.09 | 0.07 | 3.06 | 0.24 |
| PN1 | 0.85 | 2.36 | 0.01 | 1.27 | 0.10 |
| PA1 | 0.80 | 1.25 | 0.01 | 0.96 | 0.07 |
| C2 | 0.037 | 15.10 | 0.08 | 3.06 | 0.24 |
| PN2 | 0.048 | 1.37 | 0.01 | 0.99 | 0.08 |
| PA2 | 0.046 | 0.73 | 0.00 | 0.73 | 0.06 |

b) areal versions

| Model | $k_a$ or $a_a$ | f/n | $q_f$ | $d_{ma}$ | $q_d$ |
|---|---|---|---|---|---|
| C1 | 8.6 | 13.89 | 0.07 | 3.06 | 0.24 |
| PN1 | 12.7 | 3.96 | 0.02 | 1.42 | 0.11 |
| PA1 | 12.1 | 2.38 | 0.01 | 1.30 | 0.10 |
| C2 | 0.54 | 14.36 | 0.07 | 3.06 | 0.24 |
| PN2 | 0.73 | 1.38 | 0.01 | 0.93 | 0.07 |
| PA2 | 0.70 | 0.64 | 0.00 | 0.68 | 0.05 |

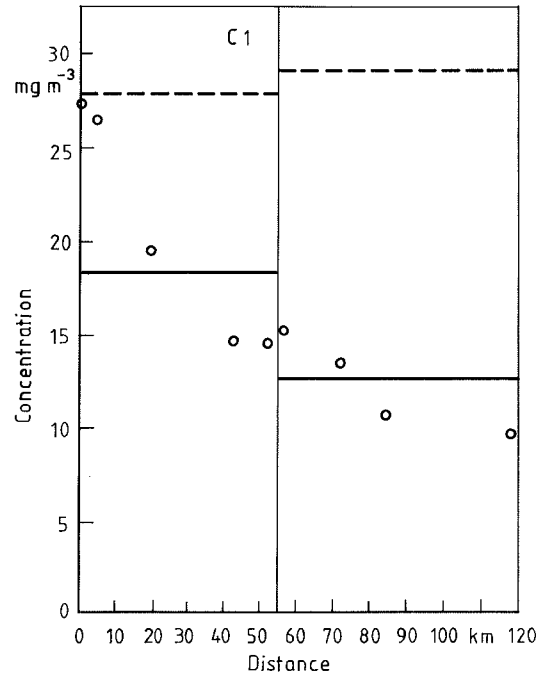
Table 28. The best combined models for Lake Päijänne as two sub-basins (average data of 1970—1973 and 1975—1986).

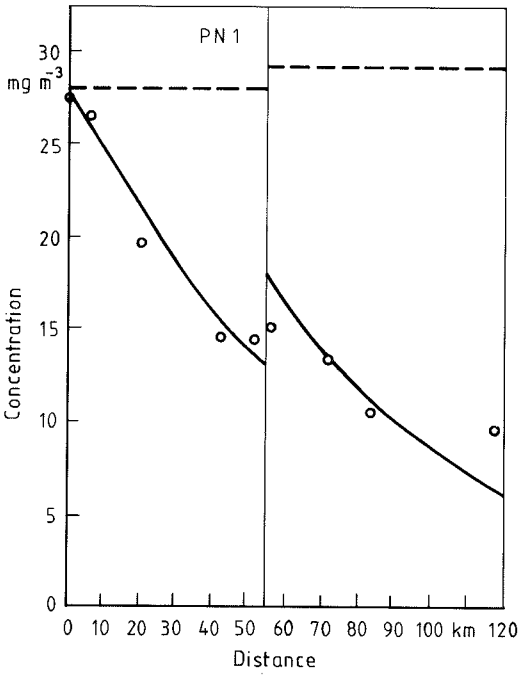
a) voluminal versions

| Model | D | k or a | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.8 | 0.81 | 1.85 | 1.11 |
| PCA1 | 0.9 | 0.79 | 1.25 | 0.94 |
| PCN2 | 1.0 | 0.050 | 1.37 | 0.99 |
| PCA2 | 1.0 | 0.046 | 0.73 | 0.63 |

b) areal versions

| Model | D | $k_a$ or $a_a$ | f/n | $d_{ma}$ |
|---|---|---|---|---|
| PCN1 | 0.8 | 12.2 | 2.75 | 1.35 |
| PCA1 | 0.9 | 11.8 | 2.21 | 1.31 |
| PCN2 | 0.9 | 0.72 | 1.28 | 0.90 |
| PCA2 | 1.0 | 0.70 | 0.64 | 0.68 |



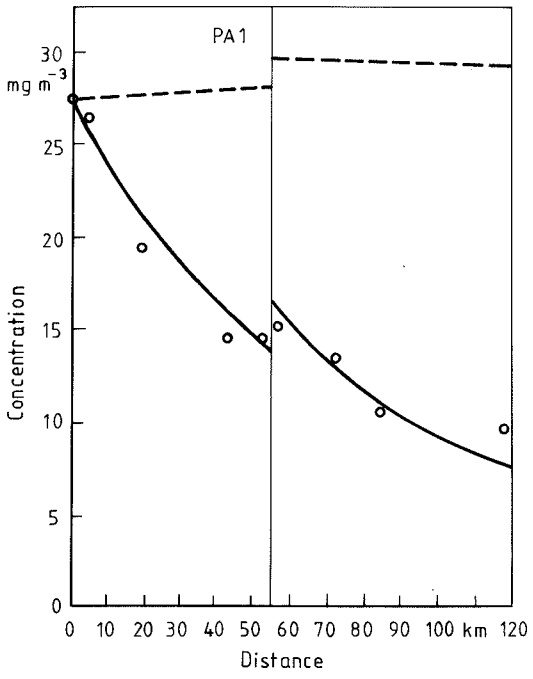




Fig. 26. Application of the first order (voluminal) modifications (C1, PN1, PA1) to Lake Päijänne as two sub-basins (average data of 1970—1973 and 1975—1986). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative modification.

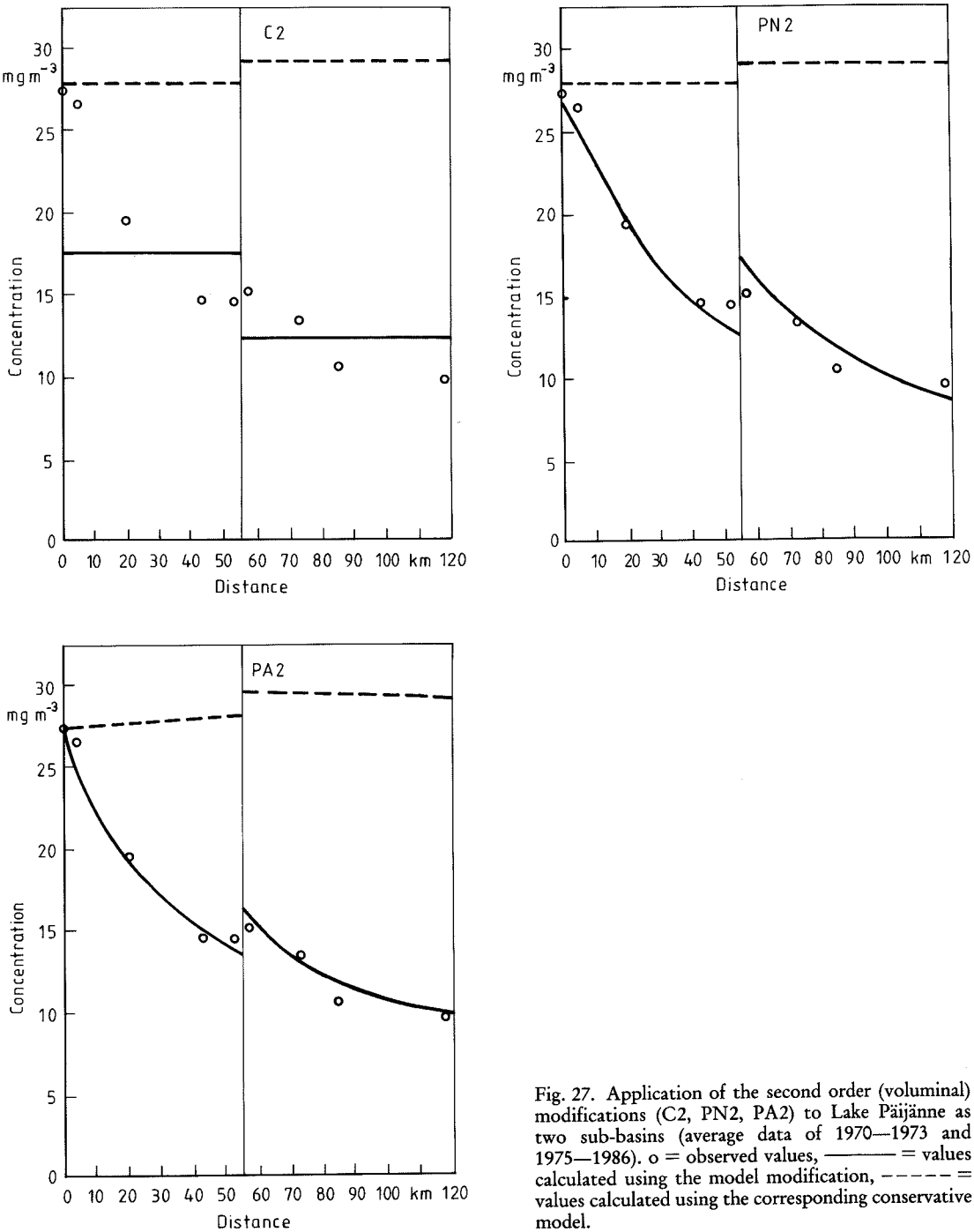



Fig. 27. Application of the second order (voluminal) modifications (C2, PN2, PA2) to Lake Päijänne as two sub-basins (average data of 1970—1973 and 1975—1986). o = observed values, ——— = values calculated using the model modification, – – – – – = values calculated using the corresponding conservative model.

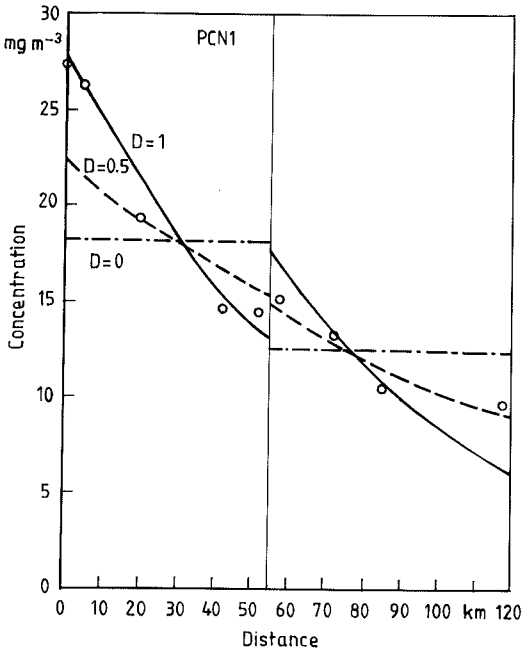



Fig. 28. Application of the combined modification PCN1 (voluminal) to Lake Päijänne as two sub-basins (average data of 1970—1973 and 1975—1986). Curves with three values of the plug flow coefficient (D) are presented, ——— = D=1 (PFR), – – – – – = D=0.5, —·—·— = D=0 (CSTR), o = observed values.

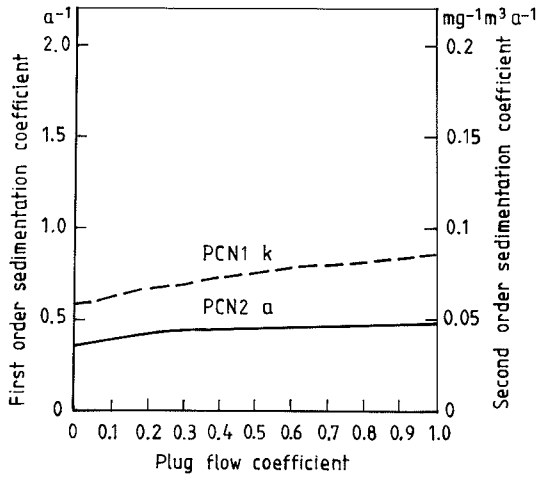



Fig. 29. The effect of the plug flow coefficient on the best sedimentation coefficient (k or a), modifications PCN1 and PCN2 (voluminal). Lake Päijänne as two sub-basins, average data of 1970—1973 and 1975—1986.

# 6 DISCUSSION

## 6.1 The effects of the basic assumptions

Steady-state mass balance modelling has been used since the 1960s. A particularly comprehensive analysis of this kind of models was made by Vollenweider (1969). It is very important to bear the steady-state assumption in mind in evaluating the results and it deserves special attention.

In lakes no real steady state can normally prevail. The mass discharges and the total amounts of substances vary with time. The term steady state in this context therefore means that during a long period of time the input, output and sedimentation conditions are assumed to remain the same, although there is, of course, variation within the period. Thus in the empirical tests of the models the average values of certain long periods must be used and correspondingly the model outputs represent average concentrations.

The minimum length of the period needed in the data can be estimated e.g. using the method presented by Dillon and Rigler (1975) who proposed that the response time can be calculated by multiplying the so-called half-life time by 3 or 5. According to Vollenweider's (1969) model (= modification C1) the half-life time is

$$t_{1/2} = \frac{\ln 2}{k + \rho} \qquad (94)$$

where
k = first order sedimentation coefficient
$\rho$ = water renewal coefficient (see Section 3.2)

The response time for Lake Päijänne would thus be 1.8—3.0 years and for Lake Haukivesi 0.5—0.9 years. Such estimations are of course approximate, but they can be used in estimating suitable time periods for steady-state applications.

Another important assumption in the models is the assumption of mixing. In CSTR modifications total mixing in all directions is assumed whereas in the plug flow modifications vertical mixing and horizontal mixing across the main stream are assumed. These assumptions are normally realistic only in the context of steady-state considerations. In dimictic lakes where the water layers are mixed twice a year the average values of the water column represent the assumed mixed concentrations at a certain point.

One problem in the empirical test of the models is the calculation of the average (observed) concentration values. In volume weighting an implicit horizontal mixing assumption is made when concentration values measured at a certain point are considered to represent a sub-basin or a certain

area. Thus the observed values cannot be considered as pure observations, but they are partly the results of a calculation procedure.

## 6.2 Applicability of the models to Lake Haukivesi and Lake Päijänne

The application of the conservative modifications revealed that it is much easier to predict the phosphorus concentration of Lake Haukivesi than of Lake Päijänne. In Lake Haukivesi the mean absolute difference between calculated and observed concentrations was only about 4 mg $m^{-3}$, whereas in Lake Päijänne it was about 13 mg $m^{-3}$. These values can be interpreted as errors that must be corrected using a sedimentation term. The description of sedimentation is usually considered to be the most difficult problem in predicting phosphorus concentration. If the data is reliable enough the conservative models including only mixing and dilution should give accurate results for conservative substances (such as chlorides).

The overall applicability of the models did not differ much between the two lakes. As a rule the f/n values (the criterion in calibrations) were smaller in Lake Haukivesi but the differences were not as great in $d_{ma}$ values. In sub-basin 1 of Lake Päijänne there is considerable variation of water quality and therefore the CSTR modifications did not give good agreement. The applicability of these modifications was especially poor in the division into two sub-basins.

In Lake Päijänne $q_f$ and $q_d$ values that express the relative success in describing the sedimentation were smaller than in Lake Haukivesi. This means that the sedimentation of phosphorus can be predicted relatively more accurately in Lake Päijänne than in Lake Haukivesi. One reason for this may be the longer detention time of Lake Päijänne.

It is not easy to decide whether the agreement between the observed and calculated values is good in an absolute sense. The values can be compared on the one hand with the accuracy of predictions needed in water management and on the other hand with the accuracy of measurements. In Lake Haukivesi the best modification gave a $d_{ma}$ value of 1.19 mg $m^{-3}$ when the whole data was used and 0.42 mg $m^{-3}$ when the average data was used. In Lake Päijänne the corresponding values were 0.90 mg $m^{-3}$ for the whole data and 0.64 mg $m^{-3}$ for the average data. The values represent the results of calibration. There were remarkable variations in the results when annual (Haukivesi) or four-yearly data (Päijänne) were used. Thus a coefficient calculated using data of one period would not necessarily give good results with the data of another period (see Appendices 3 and 4). However, if the average error is less than 1 mg $m^{-3}$ the model must be considered good and even the error value 1.19 mg $m^{-3}$ cannot be considered great from the point of view of the needs of water management.

According to the Finnish standard for measuring total phosophorus (Suomen standardisoimisliitto SFS 1986) the coefficient of variation in inland waters is between 12.2 % and 20.5 % when small concentrations (8.8—16.8 mg $m^{-3}$) are measured. The average concentrations calculated on the basis of observations do not necessarily represent the real average concentrations in the lake, because there is hardly ever sufficient data for precise estimations. However, in the average value of the whole period the problem caused by random variation is small, thanks to the great total number of observations.

## 6.3 The different modifications

In the development of the modifications the main attention was paid on the one hand to the hydraulic description of the lake and on the other hand to the order of sedimentation kinetics. In addition, both voluminal and areal versions were used. The models were applied to the lakes using two different sub-basin divisions. Thus for both lakes, 24 different single model descriptions were applied, but the combination of CSTR and PFR modifications of course increases the potential number of different models in principle to infinity, if all the different hydraulic descriptions are considered to produce a different model modification.

In the data of Lake Haukivesi the smallest f/n values were achieved using plug flow with additional input (PA1 and PA2). Of the voluminal versions the second order modification (PA2) gave the best results while of the areal versions the best results were achieved using the first order modification (PA1). Modification C1 gave surprisingly good results (f/n = 0.49, $d_{ma}$ = 0.65 mg $m^{-3}$) with the average data. The reason for this was obviously that there was only one sampling point in the northern part of Lake Haukivesi in the data. In reality there is considerable variation in water quality in this part of the lake that can be assumed to behave as a plug flow reactor rather than as a CSTR. The best combined model for Lake Haukivesi was the modification PCA2 with a value of the plug flow coefficient D=0.9 using the division into six sub-basins (with the average data f/n = 0.274,

$d_{ma} = 0.42$ mg $m^{-3}$).

Frisk (1981a, b) and Panula-Ontto-Suuronen (1987) applied a plug flow model resembling modification PN2 to Lake Haukivesi. However, the difference was that the sedimentation exponent was 1.9 instead of 2. In the study of Panula-Ontto-Suuronen (1987) the calibration was made using data of the year 1980 (f/n = 0.84, $d_{ma}$ = 0.78 mg $m^{-3}$) and validation using the data of 1979 and 1985 (f/n = 2.75, $d_{ma}$ = 1.30 mg $m^{-3}$ and f/n = 0.93 and $d_{ma}$ = 0.87 mg $m^{-3}$, respectively).

When the data of Lake Päijänne was used the best agreement between the observed and calculated results was in all cases achieved using modification PA2. Adding to the CSTR character of the lake (i.e. decreasing D from the value 1) did not decrease f/n or $d_{ma}$ values. In the data of Lake Päijänne there were two sampling points in each sub-basin. Because of the variation of water quality in the northern sub-basin CSTR modifications could not give a very realistic description. However, it is obvious that the best description of Lake Päijänne would be achieved if the northern part of the lake were described as a PFR but the southern part as partially mixed.

Frisk (1979, 1981a) developed a model for Lake Päijänne in which the lake was divided into 34 hydraulic elements and one kind of modification of second order kinetics was applied. Using this model the additional inputs could be very accurately allocated to their correct places. The model was calibrated using the data of the years 1970—1973 (f/n = 1.13, $d_{ma}$ = 0.75 mg $m^{-3}$) and validated using the data of the years 1975—1976 (f/n = 2.20, $d_{ma}$ = 1.21 mg $m^{-3}$). Because there were so many hydraulic elements the structure of the model was very close to PA modifications. Granberg (1977) reported a $d_{ma}$ value of 4.4 mg $m^{-3}$ when he applied the CSTR model of Lappalainen (1974) to Lake Päijänne. The model was applied using the coefficients presented by Lappalainen (1974).

In the evaluation of the applicability, attention must be paid not only to the objective measures of agreement between the observed and calculated values (f/n and $d_{ma}$) but also to the realism of the different modifications, especially when hydraulic description is concerned. It is possible to some extent to decide on the basis of simple observation which descriptions are realistic. Generally, the CSTR model does not apply to elongated lakes, because areal variation of water quality is normally significant. However, the division into sufficiently small sub-basins may make it possible to use CSTR modifications. Simple plug flow (i.e. plug flow with no additional input) is not realistic for lakes in which diffuse loading plays an important role. If the lake is divided into sub-basins the PN modifications lead to discontinuous concentration curves. Further it is typical of these modifications that the equilibrium concentration representing the concentration at $\tau = \infty$ is equal to zero. Thus the PA modifications can be considered to give a more realistic description in lakes where the longitudinal variation of water quality dominates. When PA modifications are used the concentration curves are continuous and the equilibrium concentrations are positive. The equilibrium concentation is $c_s$ in Eq. (45) for PA1 and $r_2$ (Eq. 60) for PA2.

In principle it is possible to apply the PA modifications to very long lakes without any sub-basin division. In order to get an analytical solution constant additional input, additional discharge and cross-sectional area are assumed. The assumption of constant additional discharge and cross-sectional area does not cause great errors in the results when the method for calculating the travel time included in these modifications is used. The error caused by the assumption of constant additional input is not very great unless there are major point-loading factors. However, in both case study lakes it was necessary to use at least two sub-basins because of the great additional input at a certain point (Tappuvirta for Lake Haukivesi and Hyrkönsalmi for Lake Päijänne). Normally, the fewer there are sub-basins the poorer is the applicability of the CSTR modifications and the PFR description is favoured.

It is not easy to decide on the basis of empirical tests whether the first or second order sedimentation kinetics should be applied or whether voluminal and areal versions are more realistic. Reckhow (1979) and Reckhow and Chapra (1983) discussed different factors affecting the phosphorus sedimentation process. According to these authors the question of whether a voluminal or an areal version is more correct is of an empirical, and not a theoretical nature because phosphorus sedimentation is a function of so many factors: hydraulic factors, phosphorus concentration, mass flow factors and also of calcium, aluminium, iron, pH, dissolved oxygen etc. In Finland the concentration of humic substances may be a very important factor in phosphorus sedimentation. When areal versions are applied, empirical data contains more information because both area and volume are included. Thus it could be assumed that the areal versions would give better agreement than voluminal. However, no great differences were found between the f/n and $d_{ma}$ values. This may be a result of the fact that there was little variation in the mean depth data.

Like the choice between voluminal and areal versions, the choice between first and second order sedimentation kinetics is also of empirical nature. The kinetic description seemed to depend on the hydraulic descriptions. When voluminal versions were concerned second order kinetics usually gave the best results in PFR models. In CSTR models first order kinetics gave better results than second. When areal versions were considered second order kinetics did not always give better results than first order kinetics in PFR models. In most cases the poorest modification was the second order CSTR model (C2).

The idea of not using first order kinetics is supported by some other studies. For example Canfield and Bachmann (1981) found the following relationship in a very large data:

$$k = k' \left(\frac{I}{V}\right)^b \qquad (95)$$

where

k = sedimentation coefficient in the sense of voluminal C1 modification ($a^{-1}$)
I = total input (mg $m^{-3}$ $a^{-1}$)
V = volume of the lake ($m^3$)
k' = coefficient (0.162 for natural lakes, 0.114 for artificial lakes and 0.129 for the whole data)
b = exponent (0.458 for natural lakes, 0.589 for artificial lakes and 0.549 for the whole data)

If it is assumed that exponent b in Eq. (95) is = 0.5, I/V as a function of the concentration can be solved applying Eg. (13):

$$\frac{I}{V} = (0.5k'c + \sqrt{(0.5k'c)^2 + \rho c}\ )^2 \qquad (96)$$

Thus according to the model of Canfield and Bachmann (1981) the retention has a second order term and a term of which the order is about two:

$$S_{ret} = 0.5k'^2c^2V + k'cV\sqrt{(0.5k'c)^2 + \rho c} \qquad (97)$$

Grobler (1985) even proposed a third order sedimentation model in which the proportionality was to the third power of the concentration.

## 6.4 The values of the coefficients

From the point of view of water management it would be most convenient if a model modification could be found in which the sedimentation coefficient would be the same in all lakes. On the basis of this study and other corresponding investigations this aim does not seem realistic.

The coefficient values for Lake Haukivesi were greater than for Lake Päijänne in all cases. When the average data or the whole data was used, the first order voluminal sedimentation coefficient k (= $\sigma$ in Vollenweider's (1969) model) varied between 1.81 and 2.25 $a^{-1}$ depending on the modification. These values were obtained using the division into six sub-basins. When the division into two sub-basins was used the C1 coefficients were smaller (from 1.30 $a^{-1}$ to 2.12 $a^{-1}$). There was considerable variation in the annual data. The smallest coefficient was 0.6 $a^{-1}$ and the greatest 4.03 $a^{-1}$ when the division into six sub-basin was used. When the division into two sub-basins was used the corresponding values were 0.43 $a^{-1}$ and 3.90 $a^{-1}$.

For Lake Päijänne the value of the voluminal first order coefficient k varied from 0.76 $a^{-1}$ to 0.86 $a^{-1}$ when the average data or the whole data and the division into four sub-basins was used and from 0.59 $a^{-1}$ to 0.85 $a^{-1}$ when the division into two sub-basins was used. The variation of the coefficient was not very great when different four-year periods were considered. The smallest value was 0.73 $a^{-1}$ and the greatest 0.89 $a^{-1}$ when the division into four sub-basins was used and the corresponding values were 0.56 $a^{-1}$ and 0.87 $a^{-1}$ when the division into two sub-basins was used. The difference in the variation compared with Lake Haukivesi can be explained by the fact that random variation can be better eliminated when four-year periods are used instead of only single years.

When the model of Canfield and Bachmann (1981) (= Eq. 95) was applied to Lake Haukivesi, the value 1.16 $a^{-1}$ was obtained using the coefficients for the whole data and the value 1.01 $a^{-1}$ using the coefficients for natural lakes (artificial lakes excluded). For Lake Päijänne the corresponding values were 0.58 $a^{-1}$ and 0.56 $a^{-1}$. These values show that differences between the coefficients of lakes Haukivesi and Päijänne can be expected on the basis of statistical analysis (Canfield and Bachmann 1981). However, only the less satisfactory CSTR hydraulics were included in this study, which may partly explain the differences between the values.

For the sake of comparison different coefficients were calculated using the data presented by Frisk (1978) and Frisk et al. (1981). In a data set consisting of 85 lakes the smallest value for k was zero and the greatest 18.21 $a^{-1}$ for Lake Raven (data published by Dillon and Rigler 1974a). The mean value was 1.72 $a^{-1}$.

The variation of the first order areal sedimentation coefficient $k_a$ (= apparent settling velocity $v$ in Chapra's (1975) study) is similar to that of the voluminal coefficient. In Lake Haukivesi using the division into six sub-basins the variation was between 19.0 m $a^{-1}$ and 24.8 m $a^{-1}$ and in the division into two sub-basins between 14.8 m $a^{-1}$ and 24.4 m $a^{-1}$. In the annual data there was great variation. The maximum value was 36.2 m $a^{-1}$ and the minimum 6.0 m $a^{-1}$ (division into two sub-basins).

For Lake Päijänne the variation of $k_a$ was between 11.4 m $a^{-1}$ and 13.1 m $a^{-1}$ in the division into four sub-basins and between 8.6 m $a^{-1}$ and 12.7 m $a^{-1}$ in the division into two sub-basins, when the whole or the average data was used. The variation between the $k_a$ values calculated using the four-year data sets was not great.

A value of $k_a$ of 16 m $a^{-1}$ was presented for the CSTR model by Chapra (1975). Vollenweider (1975) presented the value of 10 m $a^{-1}$, Dillon and Kirchner (1975) the value of 13.2 m $a^{-1}$ and Dillon the value of 12.4 m $a^{-1}$ (Chapra and Tarapchak 1976). In the data used by Frisk (1978) and Frisk et al (1981) the greatest value of $k_a$ was 57.5 m $a^{-1}$ (Lake Cameron, data presented by Dillon and Rigler (1974a)) and the smallest value was zero. Reckhow (1977) proposed the following formula for calculating $k_a$:

$$k_a = 11.6 + 0.2\frac{Q}{A} \qquad (98)$$

where
$Q$ = discharge ($m^3$ $a^{-1}$)
$A$ = area ($m^2$)

When Eq. (98) is applied the values obtained are $k_a$ = 21.1 m $a^{-1}$ for Lake Haukivesi and for $k_a$ = 13.0 m $a^{-1}$ for Lake Päijänne.

The variation of the second order coefficients was as a rule similar to the variation of the first order coefficients. The second order voluminal coefficient a varied from 0.118 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.164 $mg^{-1}$ $m^3$ $a^{-1}$ when the whole data or the average data of Lake Haukivesi, divided into six sub-basins, was used. The variation was from 0.102 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.153 $mg^{-1}$ $m^3$ $a^{-1}$ when the division into two sub-basins was used. When the annual data was used the variation was from 0.031 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.285 $mg^{-1}$ $m^3$ $a^{-1}$ (division into six sub-basins) and from 0.042 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.258 $mg^{-1}$ $m^3$ $a^{-1}$ (division into two sub-basins).

When the whole data or the average data of Lake Päijänne was used, the second order voluminal sedimentation coefficient varied from 0.045 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.050 $mg^{-1}$ $m^3$ $a^{-1}$ (division into four sub-basins) and from 0.036 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.049 $mg^{-1}$ $m^3$ $a^{-1}$ (division into two sub-basins). In the data of four-year periods the smallest variation was 0.042 $mg^{-1}$ $m^3$ $a^{-1}$ and the greatest 0.055 $mg^{-1}$ $m^3$ $a^{-1}$ when Lake Päijänne was divided into two sub-basins. Correspondingly, the smallest value was 0.035 $mg^{-1}$ $m^3$ $a^{-1}$ and the greatest 0.054 $mg^{-1}$ $m^3$ $a^{-1}$ when Lake Päijänne was divided into two sub-basins.

Frisk (1981b) and Panula-Ontto-Suuronen (1987) calibrated a plug flow model for Lake Haukivesi. In both applications the best sedimentation exponent was 1.9 and the sedimentation coefficient 0.18 $mg^{-0.9}$ $m^{2.7}$ $a^{-1}$. For Lake Päijänne Frisk (1979) obtained the value of second order voluminal sedimentation coefficient of 0.044 $mg^{-1}$ $m^3$ $a^{-1}$. Frisk (1981a) reported values of second order voluminal coefficients, part of which have been used in dynamic models. The coefficients varied from 0.11 $mg^{-1}$ $m^3$ $a^{-1}$ to 0.29 $mg^{-1}$ $m^3$ $a^{-1}$. If the data presented by Frisk (1978) and Frisk et al. (1981) is used the greatest value for a is 0.70 $mg^{-1}$ $m^3$ $a^{-1}$ (Lake Cameron, data presented by Dillon and Rigler (1974a)).

The second order areal coefficient ($a_a$) varied from 1.15 $mg^{-1}$ $m^3$ $a^{-1}$ to 1.55 $mg^{-1}$ $m^4$ $a^{-1}$ when the whole data or the average data of Lake Haukivesi, divided into six sub-basins, was used. The variation was from 1.03 $mg^{-1}$ $m^4$ $a^{-1}$ to 1.57 $mg^{-1}$ $m^4$ $a^{-1}$ when the division into two sub-basins was used. The annual variation was from 0.28 $mg^{-1}$ $m^4$ $a^{-1}$ to 2.23 $mg^{-1}$ $m^4$ $a^{-1}$ (division into six sub-basins) and from 0.26 $mg^{-1}$ $m^4$ $a^{-1}$ to 1.96 $mg^{-1}$ $m^4$ $a^{-1}$ (division into two sub-basins).

For Lake Päijänne the variation of $a_a$ was from 0.68 $mg^{-1}$ $m^4$ $a^{-1}$ to 0.76 $mg^{-1}$ $m^4$ $a^{-1}$ (division into six sub-basins) and from 0.53 $mg^{-1}$ $m^4$ $a^{-1}$ to 0.73 $mg^{-1}$ $m^4$ $a^{-1}$ (division into two sub-basins) when the whole data or the average data was used. When the four-year period data was used the corresponding variation was from 0.63 $mg^{-1}$ $m^4$ $a^{-1}$ to 0.83 $mg^{-1}$ $m^4$ $a^{-1}$ (division into four sub-basins) and from 0.49 $mg^{-1}$ $m^4$ $a^{-1}$ to 0.78 $mg^{-1}$ $m^4$ $a^{-1}$ (division into two sub-basins).

No values of the areal second order coefficients have been presented in the literature. If the data presented by Frisk (1978) and Frisk et al. (1981) is used the greatest value of $a_a$ is 7.54 $mg^{-1}$ $m^4$ $a^{-1}$ (Lake Halls, data presented by Dillon and Rigler (1974a)).

The variation within one data set results from differences between the different modifications, and especially the hydraulic description the effect of which will be discussed in the next section. The differences between the lakes are caused by the differences in the limnological character of the

different lakes. Especially in highly eutrophic lakes phosphorus retention may be very weak and thus the sedimentation coefficients calculated on the basis of empirical data are low. Reckhow (1977) developed empirical models for calculating total phosphorus concentration on the basis of phosphorus loading and hydrological and morphometric characteristics of the lake. He found that the models are different depending on e.g whether the lake is "oxic" or "anoxic". In lakes in which the hypolimnetic dissolved oxygen concentration (or rather the redox potential) is low the release of phosphorus may dominate and even in "oxic" lakes it may have a great effect (e.g. Lappalainen and Varis 1987, Lappalainen, pers.comm.).

Nürnberg (1984) modified the phosphorus model based on the use of the retention coefficient as follows:

$$c = \frac{I}{Q}(1 - R) + I_{int}\frac{A}{Q} \qquad (99)$$

where
$c$ = total phosphorus concentration (M $L^{-3}$)
$I$ = external phosphorus input (M $T^{-1}$)
$Q$ = discharge ($L^3$ $T^{-1}$)
$R$ = retention coefficient
$I_{int}$ = internal loading (M $L^{-2}$ $T^{-1}$)
$A$ = area ($L^2$)

$I_{int} \cdot A$ is equal to the release of phosphorus from the sediment $S_r$ (Eq. 8). An alternative to Eq. (99) would be the following:

$$c = c_m(k) + I_{int}\frac{A}{Q} \qquad (100)$$

where
$c_m(k)$ = total phosphorus concentration calculated using a model that includes a kinetic coefficient (k, a, $k_a$ or $a_a$)

The principal difference between Eqs. (99) and (100) is that if Eq. (99) is applied only external input is assumed to take part in the sedimentation process. In Eq. (100) sedimentation is described as a function of phosphorus concentration and thus all phosphorus in the lake affects the rate of sedimention. If internal loading can be measured accurately enough the kinetic coefficient can be calculated on the basis of observations. If not, the model should be calibrated e.g. describing $I_{int}$ as a function of hypolimnetic dissolved oxygen concentration. This approach might make it possible to obtain more universal values for sedimentation coefficients.

## 6.5 The importance of mixing

When a mass balance model is calibrated the value of the coefficient is dependent on the hydraulic description included in the model. The location of the sampling point also has an effect on the value of the coefficient. If the model is calibrated using only one sampling point that is located at the outlet of the lake or the sub-basin the calibrated coefficient will be smaller in PFR modifications than in CSTR modifications. For example for first order kinetics the explicit formulae for the coefficients are Eqs. (15) and (29). Equation (15) giving the formula for the CSTR coefficient, can be rewritten as

$$k = \frac{1}{T}\frac{c_0 - c_T}{c_T} \qquad (101)$$

For PFR the corresponding coefficient is

$$k = \frac{1}{T}\ln\frac{c_0}{c_T} = \frac{1}{T}\int_{c_T}^{c_0}\frac{dc}{c} \qquad (102)$$

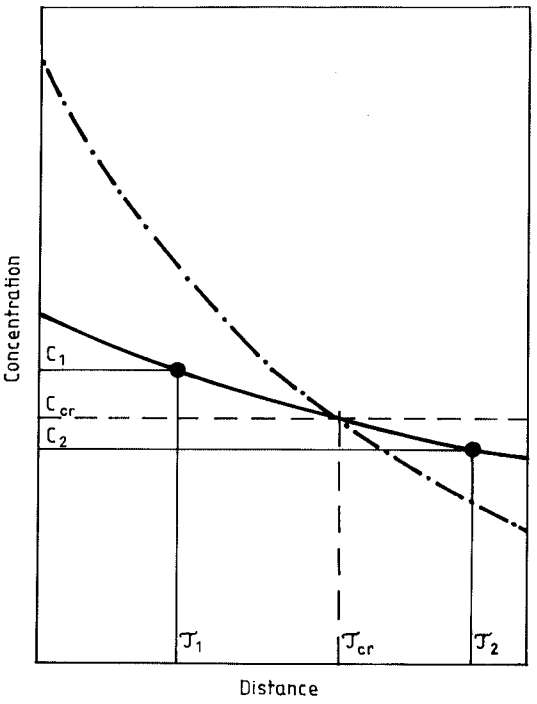



Fig. 30. Determination of the critical point in a partially mixed lake or sub-basin. $c_1$ and $c_2$ are measured concentration values. ——— = real concentration curve, – – – – – = the CSTR concentration, –·–·–·–·– = the PFR concentration.

Because the concentration decreases with the travel time and is the smallest at the outlet ($c_T$) it is clear that Eq. (102) gives smaller values than Eq. (101). However, the situation is opposite if the sampling point is located in the upper part of the sub-basin. In such cases the PFR coefficient will be greater than the CSTR coefficient.

There is a critical point for the location of the sampling station that produces the same coefficient for the CSTR and PFR models, but it is dependent on the kinetics used in the model. The location cannot be calculated if there is only one sampling point in the basin. If there are two sampling points the calculation can in principle be made using Eqs. (103)—(106) (Fig. 30).

$$c_1 = Dc_p(\tau_1,k) + (1-D)c_c(k) \quad (103)$$

$$c_2 = Dc_p(\tau_2,k) + (1-D)c_c(k) \quad (104)$$

$$c_{cr} = c_p(\tau_{cr},k) \quad (105)$$

$$c_{cr} = c_c(k) \quad (106)$$

where
$c_1$ = measured concentration at sampling point 1
$c_2$ = measured concentration at sampling point 2
$c_{cr}$ = concentration at the critical point
$\tau_1$ = travel time to sampling point 1
$\tau_2$ = travel time to sampling point 2
$\tau_{cr}$ = travel time to the critical point
D = plug flow coefficient
k = sedimentation coefficient
$c_p$ = plug flow function
$c_c$ = CSTR function

$c_1$, $c_2$ , $\tau_1$ and $\tau_2$ are measured values. The forms of the $c_p$ and $c_c$ functions are known if the sedimentation kinetics are fixed. There are four unknown variables that can be solved: $c_{cr}$, $\tau_{cr}$, k and D. If the samples are taken at the critical point (travel time $\tau_{cr}$) the coefficient calculated on the basis of measurements does not depend on the degree of mixing. This might be useful in the planning of watercourse monitoring.

As indicated by Figs. 17, 21, 25 and 29 the PFR coefficients were greater than the CSTR coefficients for both Lake Haukivesi and Lake Päijänne, but for Lake Päijänne the differences were not great. On this basis the monitoring network of Lake Päijänne can be considered rather optimal.

It is not always easy to know the degree of mixing in elongated lakes and the error in the sedimentation coefficients due to incorrect selection of the hydraulic description may cause errors when models are used in practice. This does not only concern phosphorus but the problem is the same with all substances that are modelled using this kind of approach.

An alternative way of describing partial mixing would be the use of advection-dispersion hydraulics that can also be applied in steady-state models (e.g. Chapra and Reckhow 1983). However, only first order modifications with no additional input can be used if analytical solutions are desired. In numerical solutions there may be difficulties with boundary conditions. The regulation of the degree of mixing is based on the value of the longitudinal dispersion coefficient. The value zero represents PFR, whereas the CSTR description is reached when it approaches infinity. Thus it is in a way easier to get a quantitative idea of the degree of mixing on the basis of the plug flow coefficient (varying from 0 to 1).

The degree of mixing also has an effect on the detention time of the mass ($T_m$). $T_m$ is an important factor e.g. in assessing the effects of changing loadings on lake water quality and it should be taken into account in the monitoring of recipient waters of effluents. The explicit forms for calculating detention time of the mass have been presented for most model modifications in Section 3. For the C1 modification $T_m$ is the inverse value of the extent of reaction, which Vollenweider (1975) considered to be one of the most important characteristics of the lakes. Janus and Vollenweider (1984) found a relationship between the relative residence time of phosphorus (= the detention time of phosphorus divided by the detention time of water) and the trophic condition of the lake.

For first order modifications the following relationship is valid:

$$kT_m = R \quad (107)$$

where
k = first order sedimentation coefficient ($T^{-1}$)
R = retention coefficient

Equation (107) can also be used in estimating $T_m$.

## 6.6 Sources and estimation of error

The errors are caused partly by basic assumptions (see Section 6.1) and partly by the errors in observational data. The most difficult problem is to measure the total input of substances to a lake. The problem is especially serious in cases in which diffuse loading plays an important role. The mass

discharges of rivers also vary and sufficient sampling is seldom arranged in routine monitoring.

If the variation of concentration in the lake is great there may be great errors in the estimated average concentrations, and errors may also be caused by incorrect estimation of the volume shares used in weighting. The discharge values may also be inaccurate, because they must often be based on more or less inexact water balance calculations, especially when sub-basins of a lake are concerned.

Reckhow (1979) emphasized the importance of error analysis. According to him it should become a standard routine step in comprehensive water quality management. The methods of error analysis for phosphorus models based on the retention coefficient approach have been presented e.g. by Reckhow and Chapra (1979, 1983). These authors have used variances as estimates of error for the different variables included in the models. A probabilistic approach was also applied.

Only elementary methods for estimating the magnitude of error are discussed here. The concentration is calculated using a model that is a function of total input (I), volume (V), discharge (Q) and sedimentation coefficient (k):

$$c = f_p(I, V, Q, k) \tag{108}$$

where
$f_p$ = concentration function

Correspondingly, when the sedimentation coefficient is calculated using observational data:

$$k = f_k(I, V, Q, c_o) \tag{109}$$

where
$f_k$ = coefficient function
$c_o$ = observed concentration in the lake

Differentiation produces:

$$dk = \frac{\partial f_k}{\partial I} dI + \frac{\partial f_k}{\partial V} dV + \frac{\partial f_k}{\partial Q} dQ + \frac{\partial f_k}{\partial c_o} dc_o \tag{110}$$

The error of k caused by the errors in the estimates of single factors can be approximated using partial derivatives, e.g. for input

$$\Delta k_{input} \approx \frac{\partial f_k}{\partial I} \Delta I \tag{111}$$

where
$\Delta k_{input}$ = error of k caused by the error in the input value
$\Delta I$ = error in the input value

When the concentration model is applied to a new situation (e.g. after a change of loading) the error caused by the error in the value of k can be estimated as

$$\Delta c_{k,input} \approx \frac{\partial f_p}{\partial k} \Delta k_{input} \approx \frac{\partial f_p}{\partial k} \frac{\partial f_k}{\partial I} \Delta I \tag{112}$$

where
$\Delta c_{k,input}$ = error in the predicted concentration caused by the error in coefficient k due to error in the input value

The same method can be applied to other factors (V, Q, $c_o$), e.g. for C1 the functions needed are presented by Eqs. (14) and (15):

$$f_p = \frac{I}{Q + kV} \tag{113}$$

and

$$f_k = \frac{I - Qc_o}{c_o V} \tag{114}$$

Thus the following formulae for calculating the errors can be derived:

$$\Delta c_{k,input} \approx - \frac{I}{c_o(Q + kV)^2} \Delta I \tag{115}$$

$$\Delta c_{k,volume} \approx \frac{I(I - Qc_o)}{c_o V(Q + kV)^2} \Delta V \tag{116}$$

$$\Delta c_{k,discharge} \approx \frac{I}{(Q + kV)^2} \Delta Q \tag{117}$$

$$\Delta c_{k,observed\ c} \approx \frac{I^2}{c_o^2(Q + kV)^2} \Delta c_o \tag{118}$$

The values of $\Delta c_k$ represent the errors of the predicted concentration that are caused by the errors in the estimated sedimentation coefficient, due in turn to errors in phosphorus input, volume, discharge and observational concentration data. When Eq. (108) is applied, i.e. the concentration is calculated, additional error is caused by the errors in the same data variables. Their magnitude can be estimated using the same method, as the product of the partial derivative of $f_p$ and the error of the variable. The absolute value of the total error is smaller than or equal to the sum of the absolute values of the partial errors.

Equations (115)—(118) give only approximate results. More sophisticated methods (see e.g. Reckhow and Chapra 1983) must be applied in order to obtain more exact estimates of error.

## 6.7 Kinetic mass balance models as tools in water quality management

It has been stressed that fundamental models derived from the law of conservation of mass should be used with confidence by decision makers only for objectives for which models are verified (e.g. Snodgrass 1979). In other cases the reliability of the prediction may be questioned. The traditional means of verifying a model is to apply the calibrated model using a data set that is independent of the data used in calibration. This method is suitable especially for conceptual models that describe the structure of the object system and that have many parameters to be calibrated.

The role of calibration in the sense described above is not necessarily the same when the simplest mass balance models are concerned. If a mass balance model is calibrated using data of only one year and then verified using data of one or two years, the result may be strongly affected by random factors. The models are to a great degree empirical by nature, and therefore as many years as possible should be used in the test of the model. If the variation of the sedimentation coefficient is small in different data sets (years or longer periods) the model can be expected to give reliable results in practical applications. The effect of the variation of the coefficient on predicted concentrations should be studied using sensitivity analysis. Only the application of sensitivity and error analysis can give an idea of the precision and accuracy of the predictions.

In the case lakes of this study the variation of the coefficients was very small in Lake Päijänne when different four-year periods were considered. Thus it can be stated that the calibrated models could also be used in making predictions with reasonable accuracy. In the case of Lake Haukivesi the variation of the coefficients was greater when the annual data was considered. The most probable reason is that there were too few samples in the data of one year and longer periods should be used even though the detention time and the response time (Dillon and Rigler 1975) of the lake are rather short. On the other hand Frisk (1981b) and Panula-Ontto-Suuronen (1987) found that the errors were not great when annual data of Lake Haukivesi was used by applying the same coefficient for all years.

The empirical character of this kind of simple phosphorus-balance model may give rise to the question of how great changes of water quality can be predicted using them. Reckhow (1977) found that the structure of an empirical model needed for phosphorus predictions is dependent on the characteristics of the lake, e.g. hypolimnetic oxygen concentration. Frisk (1978) and Frisk et al. (1981) studied empirical retention models and found that they do not normally give reliable results in highly eutrophic lakes. It is obvious that the same model coefficients cannot be applied if the increase of loading is so great that it totally changes the limnological character of the lake. The change in the sedimentation coefficient should then also be predicted.

The real verification of a model can be done only in strongly changing loading conditions in which the real predicting capability of the model can be studied. However, as a general rule it can be stated that the greater is the change of loading (or other) conditions the greater is the probability of errors in predictions.

If the value of the sedimentation coefficient is known the model can be used in the assessment of diffuse loading. Unfortunately the sedimentation coefficients are different in different lakes and it is not possible to calibrate the sedimentation coefficient if the total input is not known. Sensitivity to the sedimentation coefficient is a factor affecting the possibility of using this approach. If the lake is not sensitive to the sedimentation coefficient, as for example in the case of lakes with a short detention time, the models can be used to calculate the diffuse loading if the point loadings and the concentration in the lake are known.

Finally it must be stressed that the models developed and tested in this study are steady-state models that must be applied using the average data of sufficiently long periods. They cannot normally be applied as dynamic models. If e.g. the seasonal variation of concentration must be predicted the hydraulic description of the model must be more realistic. In particular the thermal stratification of the lake must be taken into account.

# 7 CONCLUDING REMARKS

1. When mass balance models are applied attention should be paid to the hydraulic description of the lake. In steady-state considerations elementary hydraulic descriptions are normally sufficient. It should be borne in mind that there are many lakes for which the most often applied description CSTR is not the best possible. Lakes that are elongated in shape may be better described using a hydraulic description that is between CSTR and PFR or even PFR.

2. In addition to the CSTR and ordinary PFR descriptions a PFR modification in which additional input along the lake is allowed can be applied. In both case lakes of this study (Lake Haukivesi and Lake Päijänne) this kind of hydraulic description usually gave the best results.
3. Using the kinetic approach it is possible to calibrate the models. In the case lakes the calibrated models gave small differences between calculated and observed phosphorus concentrations. The values of the kinetic coefficients are dependent on the order of the kinetics and on the hydraulic description and in addition they vary from lake to lake, depending on the limnological character of the lake. If there is no retention of a substance the corresponding kinetic sedimentation coefficient is equal to zero.
4. In the case lakes the best agreement between the calculated and observed phosphorus concentrations was obtained when PFR with additional input and second order sedimentation kinetics was applied. In CSTR modifications first order sedimentation kinetics gave better results than second order.
5. The value of the calibrated sedimentation coefficient is dependent on the hydraulic description selected. By combining the CSTR and PFR descriptions it is possible to develop models in which the best degree of mixing is included. The degree of mixing is regulated using the so-called plug flow coefficient the value of which is equal to 1 in PFR cases and 0 in CSTR cases. There is a critical point for taking samples that produces the same value for the sedimentation coefficient regardless of the degree of mixing. However, the location of the critical point cannot be determined unless there are at least two sampling points in the lake basin. The location of the critical point also depends on the order of the kinetics. The idea of the critical point could be utilized in rationalizing water quality monitoring networks of elongated lakes.
6. When kinetic mass balance models are calibrated, sufficiently long time periods should be used to eliminate random variation. The length of the period needed depends on the one hand on the lake, especially on the detention time and the response time of the lake and on the other hand on the sampling frequency. The models are of steady-state character and the calculated concentrations also represent average values over a long period of time.
7. The errors in the results are caused by the assumptions of the models and the errors in the observational data. The basic assumptions comprise e.g. assumptions of ideal mixing and steady state. The data needed in the models are total input of the substance, volume or surface area and discharge. For calibration data on concentration in the lake is also needed.
8. The kinetic coefficients are not universal but they should be calibrated when the model is used for making predictions. A model that has not been tested using empirical data may give unreliable results.
9. If the kinetic mass balance model is calibrated using sufficient data it can be used for making predictions in water quality management. To get an idea of the precision and accuracy of the predictions, error and sensitivity analysis should be applied. The greater the changes of the input variables are the more uncertainty there is in the predicted results.
10. Although the case study concerned only total phosphorus the method is not restricted to phosphorus. In principle all substances can be calculated if the concentration of the substance can be measured and the model can be calibrated or if the loss kinetics of the substance are otherwise known.

## ACKNOWLEDGEMENTS

First of all I wish to thank Professor Reino Ryhänen and Acting Professor Harri Seppänen under whose direction the study was performed. I also thank Professor Seppo Mustonen, Director of the Water and Environment Research Institute, Mr. Matti Raivio, Head of the Water Resources Office and Mr. Altti Luoma, Chief of the Water and Environment District of Tampere for their positive attitude towards my work. Dr. Kari Kinnunen, Mrs. Tellervo Kylä-Harakka-Ruonala and Mr. Kim Dahlbo deserve special thanks for their advice and support during the work and Dr. Erkki Alasaarela for reviewing the manuscript. I would also like to thank the personnel of the Water and Environment Districts of Kuopio and Central Finland as well as the National Board of Waters and the Environment who have helped me in collecting the data material and carrying out the documentation. Finally I thank Mr. Michael Bailey for revising the English language.

Tampere, May 1989 Tom Frisk

# YHTEENVETO

Vesistötarkkailutuloksia voidaan käyttää tehokkaasti hyväksi vasta, kun käytettävissä on menetelmiä, joilla voidaan arvioida ja ennustaa vesistöjen eri tekijöiden vaikutuksia vesistön tilaan. Vedenlaatumallit ovat tällaisia menetelmiä. Vedenlaatumallit voivat olla rakenteeltaan yksinkertaisia ainetasemalleja tai jopa hyvinkin monimutkaisia simulointimalleja.

Tässä tutkimuksessa kehitettiin yksinkertaisten ainetasemallien kokoelma, joka sisältää erityyppisiä järven kuvaamismahdollisuuksia. Osa mallimodifikaatioista on esitetty aikaisemmin, osa on kehitetty tämän tutkimuksen yhteydessä. Kehitettäessä ainetasemallia on kiinnitettävä huomiota erityisesti järven hydrauliseen kuvaamiseen sekä tarkasteltavan aineen käyttäytymiseen vesistössä.

Yksinkertaisissa vedenlaatumalleissa on tarkoituksenmukaisinta käsitellä järveä mahdollisimman yksinkertaisena hydraulisena systeeminä. Valitut hydrauliset kuvaukset olivat CSTR-kuvaus sekä kaksi eri versiota tulppavirtauksesta (PFR), joista toisessa ei tarkastella lisävirtaamaa ja -kuormitusta ja toisessa ne otetaan huomioon. CSTR edustaa täydellistä sekoittumista, kun taas tulppavirtauksessa oletetaan, että pitkittäissuuntaista sekoittumista ei tapahdu ollenkaan. Osittaista sekoittumista kuvattiin muodostamalla CSTR- ja tulppavirtausmallien lineaarinen kombinaatio, jossa sekoittumisastetta säädellään ns. tulppavirtauskertoimen avulla. Tulppavirtauskertoimen arvo 0 edustaa täydellistä sekoittumista ja arvo 1 tulppavirtausta.

Aineen pidättymistä systeemissä kuvattiin kineettisin yhtälöin. Vaihtoehtona olisi ollut ns. pidättymiskertoimeen perustuva lähestymistapa. Fosforin pidättymiskertoimen ennustamiseksi on kehitetty tilastollisia malleja, mutta niitä ei käsitelty tässä tutkimuksessa, vaan aineen pidättymistä kuvattiin ensimmäisen ja toisen kertaluvun reaktiona, ts. sedimentoituminen oletettiin suoraan verrannolliseksi joko pitoisuuteen tai sen neliöön. Tutkimuksessa tarkasteltiin kaikkien mallimodifikaatioiden tilavuus- ja pinta-alaversioita. Tilavuusversioissa sedimentaatio oletetaan verrannolliseksi järvialtaan tilavuuteen ja pinta-alaversioissa pinta-alaan.

Mallien testaamiseen käytettiin fosforitasetietoja. Fosforin valintaa voidaan perustella sillä, että riittävän edustavia fosforitasetietoja on saatavissa, fosforin kuvaaminen tällaisilla malleilla on limnologisessa mielessä järkevää ja että fosfori on tärkeä vesistöjen rehevyystasoa säätelevä ravinne. Kohdejärviksi valittiin Haukivesi ja Päijänne, jotka molemmat ovat vesiensuojelun kannalta tärkeitä tutkimuskohteita. Järvet ovat muodoltaan pitkänomaisia, joten eri mallimodifikaatioita ja erityisesti hydraulista kuvaamistapaa voidaan testata näissä järvissä. Haukivedeltä oli käytettävissä kymmenen ja Päijänteeltä kuudentoista vuoden tasetiedot. Aineistoja voidaan tässä suhteessa pitää varsin edustavina.

Sekä Haukiveden että Päijänteen ainetasetutkimuksissa järvet on jaettu osa-altaisiin. Haukiveden sovelluksessa rajattiin tutkimuksesta pois Tappuvirran itäpuolella oleva alue sekä välittömästi Varkauden alapuolella oleva alue ja Siitinselän havaintopisteen tuloksia käytettiin osa-altaaseen 1 tulevan veden pitoisuusarvoina. Haukivedessä käytettiin kahta osa-allasjakoa, joista toisessa järvi oli jaettuna kuuteen ja toisessa kahteen osa-altaaseen. Järveä ei voitu tarkastella yhtenä altaana, koska Tappuvirran lisävirtaama vaikuttaa ratkaisevasti. Myös Päijänteestä kohdealueessa oli mukana vain ns. Runko-Päijänne, ts. Lehtiselän-Tiirinselän alue oli rajattu pois. Päijännettä tarkasteltiin sekä neljänä osa-altaana että kahtena osa-altaana. Järveä ei tarkasteltu yhtenä altaana, koska Lehtiselältä tulevalla lisäkuormituksella on selvä vaikutus Keski- ja Etelä-Päijänteen veden laatuun.

Mallit kalibroitiin Haukivedelle käyttäen vuosittaista aineistoa, koko aineistoa ja koko tutkimusajan keskiarvoaineistoa. Päijänteen mallit kalibroitiin käyttäen nelivuotisjaksojen aineistoa, koko aineistoa sekä tutkimusajan keskiarvoaineistoa. Päijänteen aineistoa tarkasteltiin vuosijaksojen sijasta nelivuotisjaksoina, koska järven viipymä on pitkä (lähes kolme vuotta). Mallien kalibroinnissa käytettiin kriteerinä laskettujen ja havaittujen pitoisuusarvojen välisten erotusten neliöiden summaa. Toisena mallien hyvyyttä kuvaavana mittana käytettiin havaittujen ja laskettujen pitoisuuksien erotusten itseisarvojen keskiarvoa. Sedimentaation kuvaamisen onnistuneisuuden selvittämiseksi laskettiin myös e.m. tunnuslukujen ja vastaavalla konservatiivisella mallilla laskettujen vastaavien tunnuslukujen suhde. Konservatiivisessa mallissa sedimentaatiota ei oleteta tapahtuvan ollenkaan.

Mallien soveltuvuus Haukiveteen oli yleisesti ottaen hieman parempi kuin Päijänteeseen, mutta fosforin sedimentaatio pystyttiin Päijänteellä kuvaamaan suhteellisesti ottaen tarkemmin. Erot laskettujen ja havaittujen fosforipitoisuuksien välillä olivat yleisesti ottaen pienet. Keskiarvoaineistoa käyttäen pienin keskimääräinen virhe oli Haukivedellä 0,42 mg $m^{-3}$ ja Päijänteellä 0,64 mg $m^{-3}$. Haukiveden vuosittaisessa aineistossa mallien soveltuvuudessa ja laskettujen kertoimien arvoissa oli huomattavaa vaihtelua, kun taas Päijänteellä nelivuotisjaksoja käytettäessä vaihtelu oli vähäistä, mikä viittaa siihen, että vuosi on harvan havaintotiheyden takia liian lyhyt tarkastelujakso.

Kertoimien arvot riippuvat käytetystä kinetii-

kasta, hydraulisesta kuvauksesta sekä siitä, onko kyseessä mallin tilavuus- vai pinta-alaversio. Kineettisten kertoimien arvot olivat Haukivedellä selvästi suurempia kuin Päijänteellä. Yleensäkään kertoimien arvot eivät ole universaaleja, vaan ne riippuvat järven limnologisesta luonteesta. Esimerkiksi fosforin vapautuminen sedimentistä vaikuttaa olennaisesti sedimentaatiokertoimien arvoon.

Molemmissa järvissä sedimentaatiokertoimet olivat suurempia tulppavirtausmalleissa kuin vastaavissa CSTR-malleissa. Päijänteellä erot eivät kuitenkaan olleet yhtä suuret kuin Haukivedellä. Jos malli kalibroitaisiin luusuassa olevan havaintopisteen aineistolla, päädyttäisiin tulokseen, jossa CSTR-sedimentaatiokerroin on suurempi kuin tulppavirtaushydrauliikan sedimentaatiokerroin. Jos havaintopiste on altaan alkupäässä, tilanne on päinvastainen. On olemassa kriittinen piste, jonka havaintojen perusteella lasketun sedimentaatiokertoimen arvo ei riipu siitä, mikä sekoittumisaste on valittu malliin. Tätä seikkaa voitaisiin hyödyntää pitkänomaisten järvien tarkkailupaikkojen valinnassa.

Molemmissa kohdejärvissä tulppavirtaushydrauliikka antoi yleensä parempia tuloksia kuin CSTR. Osittain tämä selittyy sillä, että molemmissa järvissä ovat fosforipitoisuudet pohjoispäässä selvästi korkeampia kuin eteläpäässä. Paras soveltuvuus oli useimmissa tapauksissa modifikaatiolla, jossa hydraulisena kuvauksena oli lisäkuormituksen ja virtaaman huomioonottava tulppavirtaus ja sedimentaatiokuvauksena toisen kertaluvun kinetiikka. Toisen kertaluvun kinetiikka antoi yleensäkin tulppavirtauksen kanssa parempia tuloksia kuin ensimmäisen, kun taas CSTR-hydrauliikan yhteydessä ensimmäisen kertaluvun kinetiikka soveltui paremmin.

Erot laskettujen ja havaittujen arvojen välillä johtuvat mallien perusoletuksista sekä lähtötietojen virheestä. Mallien perusoletuksiin sisältyy sekoittumisoletuksia sekä tasapainotilan oletus. On korostettava, että tässä tutkimuksessa kehitetyt mallit ovat tasapainotilan malleja eikä niitä voida sellaisinaan soveltaa pitoisuuksien dynamiikan kuvaamiseen. Dynaamisissa sovelluksissa hydraulisen kuvauksen on oltava tarkempi, erityisesti terminen kerrostuneisuus on otettava huomioon. Mallin kalibroinnissa on käytettävä riittävän pitkän ajanjakson aineistoa. Tarvittavan ajanjakson pituutta voidaan arvioida järven teoreettisen viipymän ja ns. vaikutusajan (response time) perusteella.

Sovellettaessa kineettiseen lähestymistapaan perustuvaa ainetasemallia käytännössä ennusteiden laadintaan on tärkeää, että malli voidaan kalibroida riittävän luotettavalla aineistolla. Kalibroimattomalla mallilla voidaan saada harhaanjohtavia tuloksia. Käsitys ennustevirheiden suuruudesta saadaan virhetarkastelun ja herkkyysanalyysin avulla.

## LIST OF SYMBOLS

| | | |
|---|---|---|
| $a$ | = second order voluminal sedimentation coefficient | $M^{-1}\,L^3\,T^{-1}$ |
| $a_a$ | = second order areal sedimentation coefficient | $M^{-1}\,L^4\,T^{-1}$ |
| $A_i$ | = area of sub-basin i | $L^2$ |
| $A_{ri}$ | = area of the nearest drainage basin of sub-basin i | $L^2$ |
| $A_x$ | = cross-sectional area | $L^2$ |
| $c$ | = concentration of the substance considered | $M\,L^{-3}$ |
| $c_c$ | = CSTR concentration | $M\,L^{-3}$ |
| $c_{calc}$ | = concentration calculated by means of the model | $M\,L^{-3}$ |
| $c_{cr}$ | = concentration at the critical point | $M\,L^{-3}$ |
| $c_m(k)$ | = concentration calculated using a model, as a function of kinetic coefficient k | $M\,L^{-3}$ |
| $c_o$ | = observed concentration in the lake | $M\,L^{-3}$ |
| $c_{obs}$ | = observed concentration | $M\,L^{-3}$ |
| $c_p$ | = PFR concentration | $M\,L^{-3}$ |
| $c_{pT}$ | = PFR concentration at travel time T | $M\,L^{-3}$ |
| $c_{p\tau}$ | = PFR concentration at travel time $\tau$ | $M\,L^{-3}$ |
| $c_s$ | = equilibrium concentration in the PA1 modification | $M\,L^{-3}$ |
| $c_T$ | = concentration at the outlet of the basin | $M\,L^{-3}$ |
| $c_\tau$ | = concentration at travel time $\tau$ | $M\,L^{-3}$ |
| $c_0$ | = mixing concentration or concentration at travel time $\tau = 0$ | $M\,L^{-3}$ |
| $c_1$ | = measured concentration in sampling point 1 | $M\,L^{-3}$ |
| $c_2$ | = measured concentration in sampling point 2 | $M\,L^{-3}$ |
| $d_c$ | = value of $d_{ma}$ calculated using a conservative modification | $M\,L^{-3}$ |
| $d_i$ | = value of $d_{ma}$ calculated using modification i | $M\,L^{-3}$ |

$d_{ma}$ = mean absolute difference between the calculated and obseved concentrations M $L^{-3}$
D = plug flow coefficient
f = sum of the squares of the differences between the calculated and observed concentrations $M^2$ $L^{-6}$
$f_c$ = value of f calculated using a conseravtive modification $M^2$ $L^{-6}$
$f_i$ = value of f calculated using modification i $M^2$ $L^{-6}$
$f_k$ = coefficient function $T^{-1}$
$f_p$ = concentration function M $L^{-3}$
I = total input of the substance considered M $T^{-1}$
$I_{int}$ = internal loading M $L^{-2}$ $T^{-1}$
k = first order voluminal sedimentation coefficient $T^{-1}$
$k_a$ = first order areal sedimentation coefficient L $T^{-1}$
k' = coefficient of the Canfield-Bachmann model
$K_e$ = $k + S_Q/A_x$ $T^{-1}$
m = total amount of the substance considered M
$m_c$ = m calculated using the CSTR model M
$m_p$ = m calculated using the PFR model M
n = number of observations
O = total output of the substance considered M $T^{-1}$
$q_d$ = ratio of the value of $d_{ma}$ calculated using a model to that calculated using the corresponding conservative model
$q_f$ = ratio of the value of f calculated using a model to that calculated using the corresponding conservative model
$q_{ri}$ = runoff from the nearest drainage area of sub-basin i L $T^{-1}$
Q = discharge $L^3$ $T^{-1}$
$Q_i$ = outflow discharge of sub-basin i $L^3$ $T^{-1}$
$Q_K$ = discharge of Kalkkinen $L^3$ $T^{-1}$
$Q_P$ = discharge of the Päijänne tunnel $L^3$ $T^{-1}$
$Q_T$ = discharge at the outlet of the basin $L^3$ $T^{-1}$
$Q_x$ = discharge at distance x $L^3$ $T^{-1}$
$Q_0$ = initial discharge $L^3$ $T^{-1}$
$r_1$ = negative root of the equilibrium equation in PA2 modification M $L^{-3}$
$r_2$ = positive root of the equilibrium equation in PA2 modification M $L^{-3}$
R = retention coefficient
S = effect of the internal processes on the amount of substance considered M $T^{-1}$
$S_{gs}$ = gross sedimentation M $T^{-1}$
$S_I$ = additional input of the substance considered M $T^{-1}$ $L^{-1}$
$S_{ns}$ = net sedimentation M $T^{-1}$
$S_Q$ = additional input of water $L^3$ $T^{-1}$ $L^{-1}$
Sr = release from the sediment M $T^{-1}$
$S_{ret}$ = retention M $T^{-1}$
t = time T
$t_{1/2}$ = half-life time T
T = theoretical detention time T
$T_m$ = theoretical detention time of the substance T
$\bar{u}$ = average velocity of flow L $T^{-1}$
V = volume $L^3$
x = distance coordinate L
$\bar{z}$ = average depth L
$\Delta c_{k,discharge}$ = error in the predicted concentration caused by the error in coefficient k due to the error in the discharge M $L^{-3}$
$\Delta c_{k,input}$ = error in the predicted concentration caused by the error in coefficient k due to the error in the input M $L^{-3}$
$\Delta c_{k,observed\ c}$ = error in the predicted concentration caused by the error in coefficient k due to the error in the observed concentration M $L^{-3}$
$\Delta c_{k,volume}$ = error in the predicted concentration caused by the error in coefficient k due to the error in the volume M $L^{-3}$
$\Delta Q_i$ = additional flow to sub-basin i $L^3$ $T^{-1}$
$\Delta I$ = error in the input value M $T^{-1}$
$\Delta I_i$ = additional input to sub-basin i M $T^{-1}$
$\Delta k_{input}$ = error of k caused by the error in the input value $T^{-1}$
$\Delta V_i$ = volume of sub-basin i $L^3$
$\rho$ = water renewal coefficient, flushing coefficient $T^{-1}$
$\Sigma Q_{ji}$ = sum of the input discharges of the rivers $L^3$ $T^{-1}$
$\tau$ = travel time T
$\tau_{cr}$ = travel time to the critical point T
$\tau_1$ = travel time to sampling point 1 T
$\tau_2$ = travel time to sampling point 2 T

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## Appendix 1. The annual data of Lake Haukivesi

1) Total phosphorus concentrations (mg $m^{-3}$)

$c_0$ = input concentration to sub-basin 1 calculated on the basis of the sampling point at Siitinselkä and $c_2$, $c_3$, $c_4$, $c_5$ and $c_6$ = concentrations at the sampling points of the sub-basins

| Year | $c_0$ | $c_2$ | $c_3$ | $c_4$ | $c_5$ | $c_6$ |
|---|---|---|---|---|---|---|
| 1976 | 25.7 | 24.7 | 12.6 | 11.2 | 9.2 | 9.8 |
| 1977 | 19.8 | 18.3 | 11.3 | 8.7 | 8.7 | 9.7 |
| 1978 | 27.7 | 20.5 | 10.7 | 9.7 | 7.2 | 8.8 |
| 1979 | 24.5 | 21.3 | 12.8 | 11.8 | 8.0 | 7.5 |
| 1980 | 26.8 | 19.8 | 11.7 | 10.0 | 7.5 | 7.9 |
| 1981 | 18.9 | 18.6 | 13.0 | 9.5 | 7.5 | 9.5 |
| 1982 | 30.0 | 24.7 | 13.5 | 10.7 | 8.4 | 8.8 |
| 1983 | 26.2 | 22.5 | 13.8 | 10.1 | 8.6 | 9.8 |
| 1984 | 27.8 | 22.4 | 13.9 | 11.0 | 9.5 | 9.5 |
| 1985 | 28.3 | 22.6 | 14.0 | 11.8 | 8.9 | 9.5 |

2) Discharges ($m^3$ $s^{-1}$)

$Q_0$ = input discharge to sub-basin 1, $\Delta Q_1$, $\Delta Q_2$, $\Delta Q_3$, $\Delta Q_4$, $\Delta Q_5$ and $\Delta Q_6$ = additional discharge to the sub-basins, $\Delta Q_T$ = additional discharge of Tappuvirta (to sub-basin 3)

| Year | $Q_0$ | $\Delta Q_1$ | $\Delta Q_2$ | $\Delta Q_3$ | $\Delta Q_4$ | $\Delta Q_5$ | $\Delta Q_6$ | $\Delta Q_T$ |
|---|---|---|---|---|---|---|---|---|
| 1976 | 89.7 | 3.8 | 3.8 | 1.5 | 0.9 | 32.6 | 0.9 | 276.9 |
| 1977 | 131.5 | 8.6 | 8.6 | 2.3 | 1.5 | 30.5 | 1.5 | 310.2 |
| 1978 | 78.6 | 4.8 | 4.8 | 1.5 | 0.9 | 29.8 | 0.9 | 255.9 |
| 1979 | 102.7 | 8.3 | 8.3 | 1.5 | 0.9 | 34.2 | 0.9 | 292.1 |
| 1980 | 116.0 | 8.0 | 8.0 | 2.3 | 1.5 | 34.9 | 1.5 | 279.6 |
| 1981 | 186.2 | 12.2 | 12.3 | 5.4 | 3.7 | 51.3 | 3.4 | 459.6 |
| 1982 | 125.5 | 7.8 | 7.8 | 1.9 | 1.0 | 44.7 | 1.0 | 383.8 |
| 1983 | 146.7 | 9.4 | 9.2 | 3.2 | 2.1 | 48.0 | 2.1 | 404.2 |
| 1984 | 128.8 | 8.0 | 8.1 | 2.0 | 1.2 | 41.6 | 1.2 | 357.7 |
| 1985 | 103.8 | 6.6 | 6.7 | 0.7 | 1.5 | 33.5 | 1.5 | 283.5 |

3) Phosphorus inputs (mg $s^{-1}$)

$\Delta I_1$, $\Delta I_2$, $\Delta I_3$, $\Delta I_4$, $\Delta I_5$ and $\Delta I_6$ = additional inputs to sub-basins, $\Delta I_T$ = additional input of Tappuvirta (to sub-basin 3)

| Year | $\Delta I_1$ | $\Delta I_2$ | $\Delta I_3$ | $\Delta I_4$ | $\Delta I_5$ | $\Delta I_6$ | $\Delta I_T$ |
|---|---|---|---|---|---|---|---|
| 1976 | 73 | 60 | 107 | 67 | 369 | 63 | 2077 |
| 1977 | 109 | 110 | 98 | 73 | 409 | 69 | 2327 |
| 1978 | 58 | 71 | 95 | 73 | 355 | 69 | 1919 |
| 1979 | 160 | 117 | 98 | 76 | 400 | 72 | 2629 |
| 1980 | 77 | 89 | 107 | 79 | 411 | 75 | 2097 |
| 1981 | 194 | 184 | 143 | 94 | 493 | 83 | 3217 |
| 1982 | 103 | 111 | 87 | 76 | 458 | 72 | 4606 |
| 1983 | 155 | 140 | 122 | 88 | 539 | 84 | 5659 |
| 1984 | 112 | 101 | 107 | 79 | 546 | 75 | 3756 |
| 1985 | 125 | 95 | 61 | 76 | 432 | 72 | 2835 |

## Appendix 2. The four-year period data of Lake Päijänne

1) Total phosphorus concentrations (mg $m^{-3}$)

$c_0$ = input concentration to sub-basin 1, $c_{11}$, $c_{12}$, $c_{21}$, $c_{22}$, $c_{31}$, $c_{32}$, $c_{41}$, $c_{42}$ = concentrations at the sampling points of the sub-basins, the first number of the lower index indicating the sub-basin

| Period 19.. | $c_0$ | $c_{11}$ | $c_{12}$ | $c_{21}$ | $c_{22}$ | $c_{31}$ | $c_{32}$ | $c_{41}$ | $c_{42}$ |
|---|---|---|---|---|---|---|---|---|---|
| 70—73 | 32.6 | 31.8 | 22.5 | 16.3 | 15.0 | 16.3 | 15.3 | 12.3 | 10.5 |
| 75—78 | 27.8 | 26.3 | 19.1 | 15.0 | 15.0 | 15.5 | 14.0 | 10.5 | 9.8 |
| 79—82 | 25.3 | 26.0 | 18.9 | 14.8 | 14.5 | 15.5 | 13.3 | 10.0 | 10.0 |
| 83—86 | 23.5 | 21.5 | 17.0 | 12.8 | 13.5 | 13.3 | 10.5 | 9.8 | 9.0 |

2) Discharges ($m^3$ $s^{-1}$)

$Q_0$ = input discharge to sub-basin 1, $\Delta Q_1$, $\Delta Q_2$, $\Delta Q_3$ and $\Delta Q_4$ = additional discharges to the sub-basins, $\Delta Q_L$ = additional discharge from Lehtiselkä (to sub-basin 3)

| Period 19.. | $Q_0$ | $\Delta Q_1$ | $\Delta Q_2$ | $\Delta Q_3$ | $\Delta Q_4$ | $\Delta Q_L$ |
|---|---|---|---|---|---|---|
| 70—73 | 147.1 | 8.3 | 6.1 | 4.1 | 30.6 | 15.9 |
| 75—78 | 144.3 | 9.7 | 7.5 | 5.3 | 35.4 | 16.6 |
| 79—82 | 181.0 | 12.8 | 9.2 | 6.4 | 43.1 | 22.0 |
| 83—86 | 160.1 | 11.0 | 7.9 | 5.3 | 37.0 | 20.0 |

3) Phosphorus inputs (mg $s^{-1}$)

$\Delta I_1$, $\Delta I_2$, $\Delta I_3$ and $\Delta I_4$ = additional inputs to the sub-basins, $\Delta I_L$ = additional input from Lehtiselkä

| Period 19.. | $\Delta I_1$ | $\Delta I_2$ | $\Delta I_3$ | $\Delta I_4$ | $\Delta I_L$ |
|---|---|---|---|---|---|
| 70—73 | 319 | 253 | 166 | 979 | 893 |
| 75—78 | 384 | 227 | 153 | 862 | 818 |
| 79—82 | 342 | 283 | 189 | 1090 | 948 |
| 83—86 | 279 | 271 | 179 | 979 | 537 |

**Appendix 3. The results of the application of the different modifications using the annual data of Lake Haukivesi. $\bar{x}$ = mean, $s_x$ = standard deviation, $c_v$ = coefficient of variation, for other symbols see Section 5.1.**

**1 Six sub-basins**

**1.1 Conservative modifications**

| Year | CONS1 | | | CONS2 | | |
|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 1976 | 0 | 3.80 | 1.55 | 0 | 4.93 | 2.10 |
| 1977 | 0 | 4.18 | 1.70 | 0 | 4.92 | 2.12 |
| 1978 | 0 | 17.83 | 3.96 | 0 | 22.63 | 4.61 |
| 1979 | 0 | 14.59 | 3.16 | 0 | 16.73 | 3.72 |
| 1980 | 0 | 20.40 | 4.23 | 0 | 25.31 | 4.93 |
| 1981 | 0 | 3.80 | 1.64 | 0 | 2.82 | 1.27 |
| 1982 | 0 | 33.79 | 5.48 | 0 | 39.34 | 6.13 |
| 1983 | 0 | 38.75 | 5.78 | 0 | 42.65 | 6.25 |
| 1984 | 0 | 19.78 | 4.14 | 0 | 23.39 | 4.77 |
| 1985 | 0 | 20.31 | 4.13 | 0 | 24.20 | 4.80 |
| $\bar{x}$ | 0 | 17.72 | 3.58 | 0 | 20.69 | 4.06 |
| $s_x$ | 0 | 12.01 | 1.54 | 0 | 13.77 | 1.73 |
| $c_v$ | | 0.68 | 0.43 | | 0.67 | 0.43 |

**1.2 Voluminal versions**

a) first order modifications

| Year | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 1976 | 0.60 | 0.96 | 0.84 | 0.78 | 0.50 | 0.58 | 0.87 | 0.31 | 0.54 |
| 1977 | 0.99 | 0.75 | 0.83 | 1.11 | 0.86 | 0.79 | 1.19 | 0.76 | 0.77 |
| 1978 | 1.59 | 0.80 | 0.79 | 1.79 | 3.39 | 1.29 | 1.92 | 4.27 | 1.59 |
| 1979 | 1.58 | 1.37 | 1.17 | 1.91 | 0.67 | 0.72 | 1.95 | 0.63 | 0.62 |
| 1980 | 2.15 | 0.51 | 0.69 | 2.36 | 2.43 | 1.10 | 2.49 | 3.35 | 1.30 |
| 1981 | 0.89 | 2.52 | 1.28 | 1.09 | 2.34 | 1.25 | 1.13 | 1.06 | 0.89 |
| 1982 | 2.83 | 1.38 | 0.93 | 3.46 | 1.08 | 0.88 | 3.55 | 1.28 | 0.99 |
| 1983 | 3.38 | 2.71 | 1.48 | 3.99 | 2.80 | 1.31 | 4.03 | 2.72 | 1.33 |
| 1984 | 2.17 | 0.34 | 0.52 | 2.47 | 1.34 | 1.03 | 2.55 | 1.70 | 0.98 |
| 1985 | 1.74 | 0.56 | 0.64 | 1.97 | 1.84 | 1.12 | 2.04 | 2.27 | 1.09 |
| $\bar{x}$ | 1.79 | 1.19 | 0.92 | 2.09 | 1.73 | 1.01 | 2.17 | 1.84 | 1.01 |
| $s_x$ | 0.87 | 0.82 | 0.30 | 1.03 | 0.99 | 0.25 | 1.03 | 1.29 | 0.33 |
| $c_v$ | 0.49 | 0.69 | 0.33 | 0.50 | 0.57 | 0.25 | 0.47 | 0.70 | 0.33 |

b) second order modifications

| Year | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ |
| 1976 | 0.031 | 1.66 | 1.16 | 0.050 | 0.86 | 0.78 | 0.055 | 0.38 | 0.52 |
| 1977 | 0.077 | 0.99 | 0.93 | 0.096 | 0.79 | 0.82 | 0.101 | 0.48 | 0.55 |
| 1978 | 0.106 | 0.68 | 0.60 | 0.148 | 1.19 | 1.03 | 0.151 | 1.28 | 0.98 |
| 1979 | 0.103 | 2.83 | 1.62 | 0.140 | 1.25 | 1.06 | 0.140 | 0.93 | 0.84 |
| 1980 | 0.153 | 0.67 | 0.71 | 0.197 | 1.02 | 0.92 | 0.200 | 1.10 | 0.92 |
| 1981 | 0.062 | 2.81 | 1.33 | 0.086 | 2.53 | 1.27 | 0.086 | 1.22 | 0.93 |
| 1982 | 0.164 | 4.18 | 2.11 | 0.228 | 0.89 | 1.49 | 0.226 | 0.59 | 0.70 |
| 1983 | 0.219 | 4.59 | 1.66 | 0.285 | 2.02 | 1.26 | 0.280 | 1.80 | 1.18 |
| 1984 | 0.135 | 1.19 | 1.05 | 0.177 | 0.59 | 0.70 | 0.177 | 0.40 | 0.58 |
| 1985 | 0.107 | 1.25 | 0.96 | 0.140 | 0.99 | 0.90 | 0.140 | 0.84 | 0.88 |
| $\bar{x}$ | 0.116 | 2.08 | 1.17 | 0.155 | 1.21 | 0.96 | 0.156 | 0.90 | 0.81 |
| $s_x$ | 0.054 | 1.44 | 0.40 | 0.070 | 0.60 | 0.19 | 0.068 | 0.46 | 0.21 |
| $c_v$ | 0.470 | 0.69 | 0.34 | 0.453 | 0.50 | 0.20 | 0.435 | 0.51 | 0.27 |

## Appendix 3. Continued

### 1.3 Areal versions

a) first order modifications

| Year | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ |
| 1976 | 6.0 | 1.29 | 0.98 | 8.0 | 0.78 | 0.71 | 9.1 | 0.48 | 0.64 |
| 1977 | 10.8 | 0.86 | 0.90 | 12.5 | 0.85 | 0.86 | 13.4 | 0.64 | 0.70 |
| 1978 | 16.7 | 0.59 | 0.64 | 20.0 | 1.55 | 1.03 | 21.1 | 1.93 | 1.17 |
| 1979 | 16.6 | 2.10 | 1.44 | 20.5 | 0.93 | 0.91 | 21.1 | 0.59 | 0.62 |
| 1980 | 23.1 | 0.42 | 0.56 | 26.6 | 1.04 | 0.89 | 28.0 | 1.34 | 0.91 |
| 1981 | 9.1 | 2.70 | 1.31 | 11.4 | 2.51 | 1.30 | 12.0 | 1.20 | 0.96 |
| 1982 | 29.5 | 2.70 | 1.31 | 36.3 | 1.14 | 0.97 | 37.2 | 0.93 | 0.94 |
| 1983 | 36.2 | 3.97 | 1.68 | 43.0 | 2.99 | 1.60 | 43.3 | 2.71 | 1.52 |
| 1984 | 23.4 | 0.63 | 0.72 | 28.3 | 0.59 | 0.75 | 28.3 | 0.49 | 0.56 |
| 1985 | 18.6 | 0.77 | 0.69 | 22.8 | 0.88 | 0.80 | 22.8 | 0.80 | 0.75 |
| $\bar{x}$ | 19.0 | 1.60 | 1.02 | 22.8 | 1.33 | 0.98 | 23.6 | 1.11 | 0.88 |
| $s_x$ | 9.3 | 1.50 | 0.39 | 11.0 | 0.80 | 0.27 | 10.9 | 0.72 | 0.30 |
| $c_v$ | 0.49 | 0.75 | 0.38 | 0.49 | 0.60 | 0.28 | 0.46 | 0.65 | 0.34 |

b) second order modifications

| Year | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ |
| 1976 | 0.28 | 2.00 | 1.28 | 0.42 | 1.36 | 1.02 | 0.49 | 0.86 | 0.79 |
| 1977 | 0.78 | 1.20 | 0.98 | 0.96 | 0.94 | 0.93 | 1.03 | 0.55 | 0.67 |
| 1978 | 1.01 | 1.09 | 0.72 | 1.29 | 0.67 | 0.63 | 1.32 | 0.53 | 0.57 |
| 1979 | 1.01 | 3.79 | 1.83 | 1.30 | 2.21 | 1.46 | 1.31 | 1.65 | 1.24 |
| 1980 | 1.50 | 1.17 | 0.95 | 1.86 | 0.63 | 0.56 | 1.86 | 0.31 | 0.49 |
| 1981 | 0.58 | 2.99 | 1.43 | 0.83 | 2.75 | 1.32 | 0.83 | 1.42 | 0.99 |
| 1982 | 1.59 | 6.11 | 2.11 | 1.98 | 3.14 | 1.49 | 1.98 | 2.65 | 1.38 |
| 1983 | 2.23 | 6.45 | 2.08 | 2.62 | 4.06 | 1.69 | 2.62 | 3.77 | 1.62 |
| 1984 | 1.34 | 2.01 | 1.36 | 1.68 | 0.88 | 0.86 | 1.68 | 0.36 | 0.54 |
| 1985 | 1.06 | 2.02 | 1.24 | 1.33 | 1.04 | 0.76 | 1.33 | 0.51 | 0.54 |
| $\bar{x}$ | 1.14 | 2.88 | 1.40 | 1.44 | 1.77 | 1.07 | 1.44 | 1.26 | 0.88 |
| $s_x$ | 0.56 | 1.98 | 0.47 | 0.61 | 1.20 | 0.39 | 0.61 | 1.15 | 0.40 |
| $c_v$ | 0.49 | 0.69 | 0.34 | 0.45 | 0.68 | 0.37 | 0.43 | 0.91 | 0.46 |

### 2 Two sub-basins

### 2.1 Conservative modifications

| Year | CONS1 | | | CONS2 | | |
|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 1976 | 0 | 3.97 | 1.55 | 0 | 3.71 | 2.10 |
| 1977 | 0 | 4.60 | 1.83 | 0 | 4.04 | 2.12 |
| 1978 | 0 | 18.48 | 4.07 | 0 | 18.84 | 4.61 |
| 1979 | 0 | 14.92 | 3.22 | 0 | 14.80 | 3.72 |
| 1980 | 0 | 20.77 | 4.28 | 0 | 21.74 | 4.93 |
| 1981 | 0 | 3.82 | 1.64 | 0 | 3.81 | 1.62 |
| 1982 | 0 | 32.87 | 5.36 | 0 | 34.68 | 5.58 |
| 1983 | 0 | 37.46 | 5.66 | 0 | 38.85 | 5.83 |
| 1984 | 0 | 19.94 | 4.16 | 0 | 20.50 | 4.21 |
| 1985 | 0 | 20.53 | 4.15 | 0 | 21.09 | 4.19 |
| $\bar{x}$ | 0 | 17.74 | 3.59 | 0 | 18.20 | 3.62 |
| $s_x$ | 0 | 11.57 | 1.49 | 0 | 12.26 | 1.56 |
| $c_v$ | | 0.65 | 0.41 | | 0.67 | 0.43 |

## Appendix 3. Continued

### 2.2 Voluminal versions

a) first order modifications

| Year | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 1976 | 0.43 | 1.55 | 1.13 | 0.78 | 0.70 | 0.68 | 0.73 | 0.74 | 0.69 |
| 1977 | 0.76 | 0.93 | 0.79 | 1.16 | 1.04 | 0.88 | 1.10 | 0.82 | 0.81 |
| 1978 | 1.25 | 2.36 | 1.34 | 1.87 | 2.47 | 1.17 | 1.85 | 2.70 | 1.36 |
| 1979 | 1.09 | 4.27 | 1.84 | 1.93 | 0.80 | 0.73 | 2.45 | 1.06 | 0.86 |
| 1980 | 1.57 | 3.26 | 1.67 | 2.47 | 1.69 | 1.05 | 1.86 | 2.24 | 1.26 |
| 1981 | 0.45 | 3.20 | 1.39 | 1.05 | 2.51 | 1.31 | 1.00 | 2.58 | 1.26 |
| 1982 | 2.14 | 3.36 | 1.53 | 3.37 | 1.21 | 0.94 | 3.38 | 0.98 | 0.81 |
| 1983 | 2.54 | 3.36 | 1.62 | 3.90 | 3.02 | 1.56 | 3.90 | 2.63 | 1.42 |
| 1984 | 1.57 | 2.68 | 1.36 | 2.52 | 0.99 | 0.97 | 2.52 | 1.12 | 1.00 |
| 1985 | 1.24 | 3.75 | 1.77 | 2.02 | 1.42 | 1.05 | 2.02 | 1.65 | 1.17 |
| $\bar{x}$ | 1.30 | 2.88 | 1.45 | 2.09 | 1.59 | 1.03 | 2.08 | 1.65 | 1.06 |
| $s_x$ | 0.69 | 1.01 | 0.32 | 1.03 | 0.81 | 0.26 | 1.02 | 0.81 | 0.26 |
| $c_v$ | 0.53 | 0.35 | 0.22 | 0.50 | 0.51 | 0.26 | 0.49 | 0.49 | 0.25 |

b) second order modifications

| Year | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ |
| 1976 | 0.062 | 1.89 | 1.23 | 0.046 | 1.16 | 0.90 | 0.042 | 1.20 | 0.97 |
| 1977 | 0.065 | 1.07 | 0.92 | 0.097 | 1.00 | 0.94 | 0.091 | 0.80 | 0.85 |
| 1978 | 0.098 | 1.34 | 0.92 | 0.135 | 0.82 | 0.72 | 0.129 | 0.86 | 0.87 |
| 1979 | 0.082 | 4.59 | 2.04 | 0.133 | 1.65 | 1.26 | 0.125 | 1.96 | 1.38 |
| 1980 | 0.131 | 2.33 | 1.34 | 0.188 | 0.60 | 0.70 | 0.181 | 0.88 | 0.85 |
| 1981 | 0.036 | 3.26 | 1.46 | 0.080 | 2.69 | 1.33 | 0.074 | 2.77 | 1.28 |
| 1982 | 0.142 | 4.77 | 2.03 | 0.201 | 2.31 | 1.22 | 0.196 | 2.08 | 1.20 |
| 1983 | 0.182 | 4.67 | 2.07 | 0.258 | 3.30 | 1.59 | 0.252 | 3.03 | 1.50 |
| 1984 | 0.112 | 2.64 | 1.32 | 0.167 | 0.69 | 0.78 | 0.162 | 0.70 | 0.69 |
| 1985 | 0.088 | 3.26 | 1.48 | 0.132 | 0.92 | 0.73 | 0.128 | 1.08 | 0.80 |
| $\bar{x}$ | 0.096 | 2.98 | 1.48 | 0.144 | 1.51 | 1.02 | 0.138 | 1.54 | 1.04 |
| $s_x$ | 0.048 | 1.37 | 0.43 | 0.062 | 0.94 | 0.31 | 0.062 | 0.86 | 0.28 |
| $c_v$ | 0.50 | 0.46 | 0.29 | 0.43 | 0.62 | 0.31 | 0.45 | 0.56 | 0.27 |

## Appendix 3. Continued

### 2.3 Areal versions

a) first order modifications

| Year | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ |
| 1976 | 4.6 | 1.68 | 1.18 | 8.3 | 0.87 | 0.72 | 7.7 | 0.90 | 0.80 |
| 1977 | 8.6 | 1.00 | 0.85 | 13.2 | 1.03 | 0.92 | 12.4 | 0.81 | 0.82 |
| 1978 | 13.9 | 1.76 | 1.17 | 20.7 | 1.69 | 1.02 | 20.3 | 1.84 | 1.21 |
| 1979 | 12.2 | 1.00 | 4.36 | 21.2 | 1.06 | 0.95 | 20.4 | 1.31 | 1.05 |
| 1980 | 17.9 | 2.73 | 1.52 | 27.7 | 1.13 | 0.94 | 27.3 | 1.56 | 1.14 |
| 1981 | 5.0 | 3.23 | 1.43 | 11.4 | 2.61 | 1.33 | 10.7 | 2.68 | 1.28 |
| 1982 | 23.6 | 3.82 | 1.72 | 36.6 | 1.45 | 1.10 | 36.6 | 1.13 | 0.99 |
| 1983 | 28.5 | 3.99 | 1.87 | 43.2 | 3.24 | 1.65 | 43.0 | 2.82 | 1.53 |
| 1984 | 17.8 | 0.63 | 2.59 | 28.2 | 0.75 | 0.83 | 27.8 | 0.79 | 0.86 |
| 1985 | 14.1 | 3.40 | 1.63 | 22.6 | 1.08 | 0.92 | 22.2 | 1.25 | 1.05 |
| $\bar{x}$ | 14.6 | 2.86 | 1.45 | 23.3 | 1.49 | 1.04 | 22.8 | 1.51 | 1.07 |
| $s_x$ | 7.7 | 1.11 | 0.35 | 11.2 | 0.81 | 0.27 | 11.2 | 0.73 | 0.23 |
| $c_v$ | 0.52 | 0.39 | 0.24 | 0.47 | 0.55 | 0.26 | 0.49 | 0.49 | 0.21 |

b) second order modifications

| Year | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ |
| 1976 | 0.26 | 2.10 | 1.29 | 0.44 | 1.42 | 1.03 | 0.40 | 1.43 | 1.06 |
| 1977 | 0.69 | 1.21 | 1.01 | 1.03 | 1.07 | 0.98 | 0.94 | 0.87 | 0.89 |
| 1978 | 1.00 | 1.36 | 0.94 | 1.34 | 0.79 | 0.64 | 1.27 | 0.81 | 0.74 |
| 1979 | 0.86 | 4.93 | 2.12 | 1.35 | 2.26 | 1.46 | 1.26 | 2.57 | 1.58 |
| 1980 | 1.38 | 2.30 | 1.29 | 1.91 | 0.64 | 0.60 | 1.82 | 0.90 | 0.72 |
| 1981 | 0.38 | 3.39 | 1.50 | 0.80 | 2.82 | 1.34 | 0.74 | 2.89 | 1.29 |
| 1982 | 1.47 | 5.83 | 2.27 | 2.01 | 3.49 | 1.58 | 1.95 | 3.27 | 1.57 |
| 1983 | 1.96 | 5.77 | 2.31 | 2.68 | 4.41 | 1.73 | 2.60 | 4.18 | 1.66 |
| 1984 | 1.19 | 2.89 | 1.52 | 1.72 | 1.01 | 0.89 | 1.65 | 1.01 | 0.89 |
| 1985 | 0.93 | 3.36 | 1.60 | 1.36 | 1.17 | 0.80 | 1.30 | 1.32 | 0.87 |
| $\bar{x}$ | 1.01 | 3.31 | 1.59 | 1.46 | 1.91 | 1.11 | 1.39 | 1.92 | 1.13 |
| $s_x$ | 0.51 | 1.70 | 0.49 | 0.65 | 1.28 | 0.40 | 0.64 | 1.21 | 0.37 |
| $c_v$ | 0.51 | 0.51 | 0.31 | 0.44 | 0.67 | 0.36 | 0.46 | 0.63 | 0.32 |

**Appendix 4. The results of the application of the different modifications using the four-year period data of Lake Päijänne. $\bar{x}$ = mean, $s_x$ = standard deviation, $c_v$ = coefficient of variation, for other symbols see Section 5.1.**

## 1 Four sub-basins

### 1.1 Conservative modifications

| Period 19.. | CONS1 | | | CONS2 | | |
|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 70—73 | 0 | 325.75 | 16.62 | 0 | 326.32 | 16.58 |
| 75—78 | 0 | 212.99 | 13.64 | 0 | 216.96 | 13.63 |
| 79—82 | 0 | 150.94 | 11.15 | 0 | 151.49 | 11.17 |
| 83—86 | 0 | 136.96 | 10.88 | 0 | 134.60 | 10.77 |
| $\bar{x}$ | 0 | 206.91 | 13.07 | 0 | 207.34 | 13.04 |
| $s_x$ | 0 | 86.01 | 2.67 | 0 | 86.91 | 2.63 |
| $c_v$ | | 0.42 | 0.20 | | 0.42 | 0.21 |

### 1.2 Voluminal versions

a) first order modifications

| Period 19.. | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 70—73 | 0.79 | 9.02 | 2.16 | 0.89 | 4.09 | 1.68 | 0.87 | 3.15 | 1.49 |
| 75—78 | 0.73 | 4.01 | 1.42 | 0.81 | 3.78 | 1.66 | 0.80 | 2.68 | 1.28 |
| 79—82 | 0.78 | 5.24 | 1.35 | 0.89 | 2.80 | 1.42 | 0.87 | 1.81 | 1.14 |
| 83—86 | 0.75 | 2.49 | 1.26 | 0.83 | 2.28 | 1.28 | 0.81 | 1.52 | 1.02 |
| $\bar{x}$ | 0.76 | 5.19 | 1.55 | 0.89 | 3.24 | 1.51 | 0.84 | 2.29 | 1.23 |
| $s_x$ | 0.03 | 2.79 | 0.41 | 0.04 | 0.84 | 0.19 | 0.04 | 0.75 | 0.20 |
| $c_v$ | 0.04 | 0.54 | 0.27 | 0.05 | 0.26 | 0.13 | 0.05 | 0.33 | 0.17 |

b) second order modifications

| Period 19.. | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ |
| 70—73 | 0.042 | 10.85 | 2.00 | 0.048 | 1.54 | 1.08 | 0.044 | 1.04 | 0.75 |
| 75—78 | 0.043 | 4.98 | 1.41 | 0.046 | 1.67 | 1.04 | 0.046 | 1.01 | 0.83 |
| 79—82 | 0.048 | 6.80 | 1.60 | 0.053 | 2.31 | 1.07 | 0.052 | 1.59 | 0.86 |
| 83—86 | 0.053 | 2.96 | 1.12 | 0.055 | 1.07 | 0.84 | 0.054 | 0.54 | 0.58 |
| $\bar{x}$ | 0.047 | 6.48 | 1.53 | 0.050 | 1.65 | 1.01 | 0.049 | 1.05 | 0.76 |
| $s_x$ | 0.005 | 3.36 | 0.37 | 0.004 | 0.51 | 0.12 | 0.005 | 0.43 | 0.13 |
| $c_v$ | 0.10 | 0.52 | 0.24 | 0.09 | 0.31 | 0.12 | 0.10 | 0.41 | 0.17 |

## Appendix 4. Continued

### 1.3 Areal versions

a) first order modifications

| Period 19.. | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ |
| 70—73 | 11.9 | 10.39 | 2.56 | 13.6 | 5.79 | 1.85 | 13.3 | 4.74 | 1.88 |
| 75—78 | 10.9 | 4.67 | 1.74 | 12.3 | 4.69 | 1.75 | 12.2 | 3.54 | 1.37 |
| 99—82 | 11.6 | 5.52 | 1.57 | 13.5 | 3.44 | 1.52 | 13.2 | 2.38 | 1.26 |
| 83—86 | 11.2 | 3.06 | 1.53 | 12.7 | 3.00 | 1.39 | 12.3 | 2.15 | 1.20 |
| $\bar{x}$ | 11.3 | 5.91 | 1.85 | 13.0 | 4.23 | 1.62 | 12.8 | 3.20 | 1.43 |
| $s_x$ | 0.43 | 3.16 | 0.48 | 0.61 | 1.26 | 0.21 | 0.60 | 1.19 | 0.31 |
| $c_v$ | 0.04 | 0.53 | 0.25 | 0.05 | 0.30 | 0.13 | 0.05 | 0.37 | 0.22 |

b) second order modifications

| Period 19.. | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ |
| 70—73 | 0.63 | 11.00 | 2.13 | 0.68 | 1.75 | 1.15 | 0.68 | 1.22 | 0.82 |
| 75—78 | 0.65 | 4.87 | 1.38 | 0.70 | 1.58 | 1.09 | 0.69 | 0.92 | 0.89 |
| 79—82 | 0.72 | 6.55 | 1.57 | 0.80 | 2.17 | 1.11 | 0.79 | 1.44 | 0.88 |
| 83—86 | 0.79 | 2.97 | 1.16 | 0.84 | 1.06 | 0.85 | 0.83 | 0.50 | 0.57 |
| $\bar{x}$ | 0.70 | 6.35 | 1.56 | 0.76 | 1.64 | 1.05 | 0.75 | 1.02 | 0.79 |
| $s_x$ | 0.07 | 3.43 | 0.41 | 0.78 | 0.46 | 0.14 | 0.73 | 0.41 | 0.15 |
| $c_v$ | 0.10 | 0.54 | 0.27 | 0.10 | 0.28 | 0.13 | 0.10 | 0.40 | 0.19 |

### 2 Two sub-basins

### 2.1 Conservative modifications

| Period 19.. | CONS1 | | | CONS2 | | |
|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 70—73 | 0 | 321.93 | 16.58 | 0 | 324.17 | 16.54 |
| 75—78 | 0 | 206.64 | 13.41 | 0 | 213.50 | 13.51 |
| 79—82 | 0 | 149.19 | 11.07 | 0 | 150.68 | 11.15 |
| 83—86 | 0 | 139.87 | 11.07 | 0 | 134.81 | 10.80 |
| $\bar{x}$ | 0 | 204.41 | 13.03 | 0 | 205.79 | 13.00 |
| $s_x$ | 0 | 83.73 | 2.61 | 0 | 85.93 | 2.65 |
| $c_v$ | | 0.41 | 0.20 | | 0.42 | 0.20 |

## Appendix 4. Continued

### 2.2 Voluminal versions

a) first order modifications

| Period 19.. | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ | k | f/n | $d_{ma}$ |
| 70—73 | 0.60 | 24.90 | 3.98 | 0.87 | 4.33 | 1.58 | 0.83 | 2.60 | 1.49 |
| 75—78 | 0.56 | 13.53 | 3.08 | 0.79 | 3.07 | 1.43 | 0.76 | 1.69 | 1.13 |
| 79—82 | 0.59 | 14.24 | 3.05 | 0.87 | 2.47 | 1.38 | 0.83 | 1.45 | 1.06 |
| 83—86 | 0.59 | 7.36 | 2.26 | 0.83 | 2.66 | 1.41 | 0.78 | 0.94 | 0.81 |
| $\bar{x}$ | 0.59 | 15.01 | 3.09 | 0.84 | 3.13 | 1.45 | 0.80 | 1.67 | 1.12 |
| $s_x$ | 0.02 | 7.28 | 0.70 | 0.04 | 0.83 | 0.09 | 0.04 | 0.70 | 0.29 |
| $c_v$ | 0.04 | 0.49 | 0.23 | 0.05 | 0.27 | 0.06 | 0.095 | 0.42 | 0.26 |

b) second order modifications

| Period 19.. | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ | a | f/n | $d_{ma}$ |
| 70—73 | 0.035 | 26.31 | 3.98 | 0.043 | 2.27 | 1.11 | 0.041 | 1.54 | 0.87 |
| 75—78 | 0.035 | 14.35 | 3.08 | 0.040 | 1.38 | 0.99 | 0.043 | 0.81 | 0.73 |
| 79—82 | 0.038 | 15.35 | 3.09 | 0.051 | 2.15 | 1.24 | 0.049 | 1.71 | 0.86 |
| 83—86 | 0.043 | 8.03 | 2.40 | 0.054 | 1.39 | 0.94 | 0.051 | 0.37 | 0.45 |
| $\bar{x}$ | 0.038 | 16.01 | 3.13 | 0.047 | 1.79 | 1.07 | 0.046 | 1.11 | 0.73 |
| $s_x$ | 0.004 | 7.59 | 0.65 | 0.007 | 0.48 | 0.13 | 0.005 | 1.00 | 0.20 |
| $c_v$ | 0.11 | 0.47 | 0.21 | 0.14 | 0.27 | 0.12 | 0.10 | 0.57 | 0.27 |

### 2.3 Areal versions

a) first order modifications

| Period 19.. | C1 | | | PN1 | | | PA1 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ | $k_a$ | f/n | $d_{ma}$ |
| 70—73 | 8.8 | 24.80 | 3.98 | 13.0 | 6.77 | 2.11 | 12.4 | 4.78 | 2.07 |
| 75—78 | 8.1 | 13.57 | 3.10 | 11.8 | 4.47 | 1.62 | 11.4 | 2.93 | 1.35 |
| 79—82 | 8.6 | 13.62 | 3.05 | 13.0 | 3.20 | 1.46 | 12.4 | 2.01 | 1.19 |
| 83—86 | 8.6 | 7.28 | 2.15 | 12.5 | 3.62 | 1.62 | 11.6 | 1.68 | 1.04 |
| $\bar{x}$ | 8.5 | 14.82 | 3.07 | 12.6 | 4.52 | 1.70 | 12.0 | 2.85 | 1.41 |
| $s_x$ | 0.30 | 7.29 | 0.74 | 0.59 | 1.59 | 0.28 | 0.54 | 1.39 | 0.46 |
| $c_v$ | 0.03 | 0.49 | 0.24 | 0.05 | 0.35 | 0.16 | 0.04 | 0.49 | 0.32 |

b) second order modifications

| Period 19.. | C2 | | | PN2 | | | PA2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ | $a_a$ | f/n | $d_{ma}$ |
| 70—73 | 0.49 | 25.32 | 3.98 | 0.65 | 2.53 | 1.07 | 0.63 | 1.65 | 0.96 |
| 75—78 | 0.50 | 13.73 | 3.08 | 0.67 | 1.42 | 1.02 | 0.65 | 0.78 | 0.84 |
| 79—82 | 0.55 | 14.45 | 3.05 | 0.77 | 1.91 | 1.12 | 0.74 | 0.74 | 0.82 |
| 83—86 | 0.63 | 7.54 | 2.31 | 0.82 | 1.39 | 0.95 | 0.78 | 0.27 | 0.41 |
| $\bar{x}$ | 0.55 | 13.71 | 3.10 | 0.73 | 1.81 | 1.04 | 0.70 | 1.02 | 0.76 |
| $s_x$ | 0.06 | 7.27 | 0.68 | 0.08 | 0.53 | 0.07 | 0.07 | 0.62 | 0.24 |
| $c_v$ | 0.15 | 0.53 | 0.22 | 0.12 | 0.29 | 0.07 | 0.10 | 0.61 | 0.32 |